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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

1. Analytical aspects of some azo dyes from chromotropic acid. VI. Analytical reactions of some 'SNADNS' dyes. S. K. Datta (Victoria Coll., Coochbehar, West Bengal, India). *Z. anal. Chem.*, 1959, **167** (2), 105-110 (in English).—Certain azo dyes prepared from chromotropic acid and aromatic amines (*Naturwissenschaften*, 1956, **43**, 250), in the form of 0.05% soln. on filter-paper are proposed as spot reagents for Th^{IV} , Fe^{III} , Zr^{IV} and Ce^{IV} also give colours, but these are less marked and less stable. As little as $3 \mu\text{g}$ to $4 \mu\text{g}$ of Th^{IV} can be detected. The composition of the dyes is given.

H. M.

2. Spectrophotometric investigation of the analytical reagent 1-(2-pyridylazo)-2-naphthol (PAN) and its copper chelate. B. F. Pease and M. B. Williams (Oregon State Coll., Corvallis, U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1044-1047.—The absorption spectra of the three forms of PAN at various pH values in H_2O and 20% dioxan, and the absorption spectrum of the Cu^{2+} -PAN chelate at pH 5 in 20% dioxan, are reported. The equilibrium forms, dissociation constants, effects of pH and of various solvents, metal-chelate ratios and stabilities are discussed. For the neutral yellow form (HKE), the equilibrium constant for the reaction $\text{HKE} + \text{Cu}^{2+} \rightleftharpoons \text{CuKE}^+ + \text{H}^+$ is 6.4×10^9 , and the stability constant for the 1:1 chelate is $\approx 10^{10}$, in comparison with 2×10^{10} for the corresponding Cu-EDTA complex.

W. J. BAKER

3. Acid-base titrations in acetic anhydride. R. Reiss (Fa. Byk-Gulden Lomberg, Chem. Fabrik G.m.b.H. Konstanz/Bodensee). *Z. anal. Chem.*, 1959, **167** (1), 16-27.—A wide range of weak bases and salts was titrated in acetic anhydride with 0.1 N HClO_4 in anhyd. glacial acetic acid soln., with crystal violet as indicator. Of the compounds studied, many were initially sol. in the medium, some dissolved rapidly during titration, and others were almost insol. and gave very long titration times. This was overcome by first dissolving the compound in formic acid, and then adding a large excess of acetic anhydride before titration. Some compounds, e.g., xanthen derivatives, hydrogen halide salts, and alkali, alkaline-earth and ammonium halide salts of organic bases, which cannot be titrated in glacial acetic acid, can be titrated in acetic anhydride. Sulphates react as monohydric acids and therefore hydrogen sulphates cannot be titrated. Nitrates and nitrites interfere with the indicator. Quoted results are within accepted limits of error. The mechanism of the acid-base exchange reactions that occur is discussed.

S. M. MARSH

4. Omega Chrome Fast Blue 2G: a new metal indicator for EDTA titrations. A. A. El Raheem (Public Health Lab., Cairo, Egypt). *Z. anal. Chem.*, 1959, **167** (2), 98-104 (in English).—Omega Chrome Fast Blue 2G (C.I. Mordant Blue 44) gives pink to violet colours with Ca^{II} , Mg^{II} , Mn^{II} , Ni^{II} , Ce^{III} , Ce^{IV} and Co^{II} . This is proposed as a basis for spot tests for these metals. The sensitivity is increased if mucilage of fenugreek is added. The pH is kept at 10 by means of aq. NH_3 - NH_4Cl buffer, and a little tartaric acid is added to keep certain metals in solution. The sensitivity of the dyestuff to metal ions enables Mg^{II} , Ca^{II} and Mn^{II} to be titrated with 0.01 M EDTA (disodium salt) at pH 10 at room temp., while Ni^{II} can be titrated at 80° and pH 8-35. A little ascorbic acid prevents pptn. of Mn^{II} . The colour change is from wine-red to blue. By the use of a 1% soln. of manganese-EDTA, Pb^{II} and Cd^{II} can be titrated.

H. M.

5. Diacridyl derivatives as chemiluminescent indicators. E. Michalski and M. Turowska (Dept. of Inorg. Chem., Łódź Univ., Poland). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 599-607.— NN' -Dipropyl, NN' -di-*p*-tolyl, NN' -diphenyl and NN' -diallyl diacridyl dinitrates are used as luminescent indicators for the direct and back-titration of strong acids with strong bases. The results are compared with those obtained with phenolphthalein and bromothymol blue as indicators. The addition of aliphatic alcohols (methanol, ethanol, *n*-propanol and isobutyl alcohol) diminishes the relative error as compared with the result obtained with bromothymol blue.

H. DMOWSKA

6. Analytical chemical studies in ultra-violet light. II. Some new fluorescent adsorption indicators. J. Bognár (Tech. Univ. f. Schwerind., Miskolc, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1959, **20** (1), 103-112 (in German).—New fluorescent indicators for precipitation titrations in u.v. light are described. Ethacridine lactate is suitable for the titration of halogens with AgNO_3 , and the product obtained by oxidising Trypan red (C.I. 22850) with Ce^{4+} or MnO_4^- is suitable for the titration of halogens, isocyanide or silver ions. Riboflavine and Aurazin G (C.I. Basic Yellow 6) may be used for the titration of isocyanide and silver ions. Indigosol blue IBC (C.I. Solubilised Vat Blue 6) gives good results for the titration of isocyanide, bromide and iodide, but not chloride. An advantage of riboflavine and indigosol blue is that they can be used in acid solution. Typical results are tabulated.

S. M. MARSH

7. High-precision titrimetry. I. An examination of the attainable precision. E. Bishop (The Univ., Exeter, England). *Anal. Chim. Acta*, 1959, **20** (4), 315-323.—The precision attainable with volumetric apparatus is critically assessed and detailed consideration is given to burette-drainage errors.

Precision can be improved by the use of weight-titrimetric and pipette-dilution methods, but limitations are imposed by the purity of reagents and the errors of end-point detection. H. N. S.

8. Acidimetry in non-aqueous medium. I. Basis of the method. J. A. Gautier (Fac. de Pharm., Paris, France). *Bull. Soc. Chim. France*, 1959, (2), 279-282.—A review is given of the theories of acidity and basicity, and the effect of solvents, both amphiprotic and aprotic, on the titratable acidity or basicity.

II. Techniques and applications. F. Pellerin. *Ibid.*, 1959, (2), 283-287.—A review is given of the practicable methods of determination of acids and bases in non-aqueous solvents. E. J. H. BIRCH

9. Radiochemical titration with labelled potassium ferrocyanide volumetric solution. G. Tölgyessy (Radiochem. Inst., Bratislava, Czechoslovakia). *Magyar Kém. Foly.*, 1959, **65** (4), 149-152.—The determinations are based on the formation of insol. ferrocyanides by the heavy metals; the composition of these ppt. depends on the alkali metal present. The titrations were carried out either by the classical method or by preparing a series of mixtures from the unknown and various amounts of 0.025 M $K_4^{109}Fe(CN)_6$ and centrifuging them. A 0.2-ml aliquot from each supernatant liquid is placed on a circular filter-paper, and the activity of the dried spots is measured automatically on a Frieske & Hoepfner FH Automat. The end-point is determined from the titration curve (obtained from the activities) or by calculation. By this method, Zn^{2+} , Pb^{2+} , Ag^+ and (in aq. NH_3) Cu^{2+} can be determined. In the simultaneous determination of Zn^{2+} and Pb^{2+} , the two are determined together, then Zn^{2+} are determined in a second sample after pptg. Pb^{2+} with H_2SO_4 . Anions that give an insol. ppt. with Pb^{2+} (e.g., SO_4^{2-} , CO_3^{2-} , CrO_4^{2-} , F^- , IO_3^- , oxalate) are determined by pptg. them with a known vol. of standard $Pb(NO_3)_2$ soln. and back-titrating the excess of Pb^{2+} . A. G. PETO

10. Chelating properties of NNN'-tetrakis(phosphonomethyl)-1:2-diaminocyclohexane [cyclohexanediaminetetramethylphosphonic acid, CDTMP]. C. V. Banks and R. E. Yerick (Iowa State Coll., Ames, U.S.A.). *Anal. Chim. Acta*, 1959, **20** (4), 301-314.—The preparation of the octasodium salt of this reagent is described and the eight pK values are derived from a titration curve of the free acid with NaOH soln. Stability constants are determined for complexes of the reagent with Mg, Ca, Sr, Ba, Zn, Cd, Hg^{2+} , Pb, Mn^{2+} , Cu^{2+} , Co^{2+} , Ni and Fe^{3+} . The titration of Fe^{3+} is possible in acid soln. (pH ≈ 1.5) with sulphosalicylic acid as indicator, but the end-point is poor. The other metals do not form complexes of stability suitable for purposes of titration. H. N. S.

11. Indirect methods in flame photometry. J. Malinowski (Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 549-553.—The influence of accompanying substances upon the emission of the alkaline-earth metals in the air-acetylene and oxy-hydrogen flames is discussed. Methods are given for the determination of PO_4^{3-} , SO_4^{2-} , AsO_4^{3-} , Be, Zr and Al by means of the reduction in intensity of the calcium emission.

H. DMOWSKA

12. The application of X-ray diffraction methods of identification of crystalline phases in chemical analysis. A. Janko and Z. Zagórski (Central Lab.

of Accumulators and Cells, Poznań, Poland). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 561-565.—X-ray diffraction is used for the structural analysis of lead compounds in the analysis of ores, corrosion sediments, etc., and in checking the composition of metal powders (e.g., Cd, Cu, Zn and Fe) obtained by electrolysis. H. DMOWSKA

13. Mass spectra of some organic and inorganic compounds. A. S. Newton and S. J. Waters (Lawrence Radiation Lab., Univ., Berkeley, Calif.). *U.S. Atomic Energy Comm., Rep. UCRL-8654*, 1959, 50 pp.—A compilation is made of some mass spectra of various organic and inorganic compounds (collected from various sources) which are not listed in previous compilations of mass-spectral data. All have appreciable vapour pressures at room temp. and were run with a room-temp. inlet system on a Consolidated Engineering Corporation Model 21-103 analytical mass spectrometer; a few were run on Model 21-102. NUCL. SCI. ABSTR.

See also Abstracts—16, 111. Titrations with chromous acetate. 131. Diphenylthiovioluric acid as reagent.

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

14. Titrations with hydrogen peroxide and sodium hypobromite solutions. L. Erdey and J. Inczédy (Inst. f. Allg. Chem. der Tech. Univ., Budapest). *Z. anal. Chem.*, 1959, **166** (6), 410-417.—In alkaline soln., $Ni(OH)_2$ is oxidised by OBr^- to the strongly coloured $Ni(OH)_3$. It is shown that this change from pale green to black may be used as an indicator for titrations with OBr^- or H_2O_2 . Excess of OBr^- may be determined by titration with H_2O_2 , and this has been applied to the determination of S^{2-} , SO_3^{2-} , $S_2O_3^{2-}$, AsO_3^{3-} and NH_4^+ by adding a measured vol. of OBr^- soln. and 3 drops of indicator soln. (5% aq. $NiSO_4 \cdot 7H_2O$ soln.) to the alkaline soln. and titrating the excess of OBr^- with standard H_2O_2 soln. By addition of KBr to liberate OBr^- , OCI^- may be determined in a similar fashion. A precision of $\approx 1\%$ is claimed. T. R. ANDREW

15. Determination of oxygen, hydrogen and nitrogen in refractory metals. J. E. Fagel, R. F. Witbeck and H. A. Smith (Gen. Electric Co., Cleveland, Ohio, U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1115-1116.—The gaseous elements in molybdenum, tungsten, tantalum and molybdenum-titanium alloy (0.5% of Ti) can be determined by dropping the sample (0.2 to 2 g) into a bathless outgassed crucible at 2000° and analysing manometrically the gases collected during 20 to 30 min. by vacuum extraction at this temp. The results compare well with those obtained by the vacuum fusion method with an iron-tin bath. The advantages claimed include a fourfold saving in time, smaller blanks, and less initial preparation of the sample. W. J. BAKER

16. Reductimetric determination of metals in non-aqueous media. J. Minczewski, S. Kolyga and I. Wódkiewicz (Inst. Badań Jądrowych, Warsaw). *Nukleonika*, 1958, **3** (Spec. No.), 62-66 (in English).—Chromous acetate (I) is used in the reductimetric determinations of U, V and Cu. Soln. of uranyl

nitrate (containing 10 mg of U) in 30 ml of ethanol were acidified with 0.5 ml of conc. H_2SO_4 and titrated with 0.02 N I in dioxan. Tributyl phosphate or ethyl acetate can also be used as the solvent. Copper (1 mg per ml) and V (0.2 mg per ml) were extracted with a 0.15% soln. of 8-hydroxyquinoline in $CHCl_3$. A mixture (1:1, v/v) of methanol and conc. H_2SO_4 or $HClO_4$, at a ratio of 0.5 ml to 30 ml of soln., was added and the soln. titrated as before. Titration curves of soln. containing Cu and V show two inflection points corresponding to the reduction of V^{IV} to V^{III} and to the sum of the reductions of V^{IV} to V^{III} and Cu^{II} to Cu^I , which occur at about the same potential. If soln. were not acidified, Cu bound in the complex was not reduced and V was reduced only to V^{IV} . CHEM. ABSTR.

17. Acidimetric titration of metal acetates in glacial acetic acid. A. T. Casey and K. Starke (Dept. of Chem., Univ. of British Columbia, Vancouver). *Anal. Chem.*, 1959, **31** (6), 1060-1062.—The acetates of Na, K, NH_4^+ , Li, Mg, Ca, Ba, Sr, Zn, Cd, Mn, Co, Ni, Ag and Pb in glacial acetic acid (0.075 N) can be titrated with 0.1 N $HClO_4$ in glacial acetic acid. The titration can be made potentiometrically or with a visual end-point (crystal violet as indicator). The accuracy is comparable with that for the usual analytical methods. The acetates of Al, Fe, Cr, Cu, Sn, Sb, Bi and U cannot be titrated in this way. For the titration of Co and Ni, a soln. of $HClO_4$ in dioxan must be used. Not more than 1.5% of H_2O must be present.

W. J. BAKER

18. Micro-analysis of metals by optical emission spectroscopy. E. F. Runge and F. R. Bryan (Ford Motor Co., Dearborn, Mich., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (3), 74-76.—A micro-drill of 6.4 μ diameter has been used to remove 2×10^{-6} g portions from a sample. With such quantities in the Littrow quartz spectrograph (speed 1/26) and with Eastman 103-O emulsion the limit of detectability for Fe, Al, Cu, Cr and Pb is $\approx 1 \times 10^{-6}$ g. The drilling technique, sample manipulation and spectrographic sensitivity are discussed and the possibility of improvement is predicted.

E. G. CUMMINS

19. Infra-red spectra of metal nitrates. F. Vratny (Dept. of Chem., Purdue Univ., Lafayette, Ind., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (3), 59-70.—The spectra of the nitrates of Li, Na, K, Rb, Cs, Cu, Ag, Be, Mg, Ca, Sr, Ba, Bi, Cr, Mn, Zn, Cd, Hg, Pr, Nd, Sm, Gd, Al, Y, La, Ce, Th, Pb, Fe, Co and Ni are illustrated. It is concluded from the changes in absorption in the 1360- and 1050- cm^{-1} regions that inferences can be made regarding the type of bonding between the metal ion and the nitrate group. From this it is shown that the rare-earth-metal nitrates, thorium tetranitrate, and chromium, nickel and mercurous nitrates exhibit a certain degree of covalent metal-to-nitrate bonding. The remainder exhibit ionic metal-to-nitrate bonds.

E. G. CUMMINS

20. Half-wave potentials of metal ions in organic hydroxy acid supporting electrolytes. II. S. Baumgarten, R. E. Cover, H. Hofmann, S. Karp, P. B. Pinches and L. Meites (Polytech. Inst. of Brooklyn, N.Y., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (4), 397-404.—Information is presented on the E_1 , reversibilities, wave shapes, and probable electrode reaction products for the polarographic waves of most of the common heavy-metal ions in

0.1 M ammonium citrate at pH 6 and in 0.1 M ammonium citrate, malonate, oxalate or tartrate containing 0.1 N aq. NH_3 . H. N. S.

21. Chelometric determination of chromium, cobalt(III) and copper with a metalfluorechromic indicator. D. H. Wilkins (General Electric Res. Lab., Schenectady, N.Y., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (4), 324-325.—The fluorescent metal indicator calcein is used for the titration of the three metals in view of the intense colours of their EDTA complexes. A slightly acid soln. of Cr^{3+} (20 to 40 mg) is treated with an excess of EDTA, the pH is adjusted to 4.5 with Na acetate-acetic acid buffer, the soln. is diluted to 150 ml and boiled for 15 min.; 1 drop of indicator soln. (0.1% in 0.001 N NaOH) is added and back-titration is carried out with a standard soln. of Cu^{2+} . Cobalt (21 to 64 mg) is oxidised to Co^{3+} with H_2O_2 in a soln. buffered at pH 9.5 with NH_4Cl and aq. NH_3 , an excess of EDTA is added and the excess is titrated with a standard soln. of Cu^{2+} . Solutions of Cu^{2+} (47 to 57 mg) are treated with an excess of EDTA at pH 4.5 to 9.5 and, after diluting to 150 ml, the excess is titrated with a standard soln. of Cu^{2+} .

H. N. S.

22. Phthalocyanines as oxidation-reduction indicators. V. Titration of iron(II), uranium(IV) and molybdenum(V) with sodium vanadate. G. Gopala Rao and T. P. Sastri (Dept. of Chem., Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1959, **167** (1), 1-8 (in English).—The use of a 0.1% soln. of Cu-PTS (copper phthalocyaninetetrasulphonic acid) (I) as a redox indicator in vanadimetry has been investigated. Tabulated observations show the effect of Fe^{III} and V^{IV} salts on the reaction between vanadic acid and I in H_2SO_4 and HCl media. The colour change takes place more rapidly in HCl ; Fe^{3+} accelerate the reaction, but V^{4+} retard it in concn. up to 12 N H_2SO_4 and 6 N HCl . The effect of V^{4+} can be overcome by the addition of 3 ml of syrupy H_3PO_4 for each 60 ml of titration mixture. Bivalent Fe, U^{IV} and Mo^{IV} may be titrated with sodium vanadate soln. in 12 N H_2SO_4 with the addition of 3 ml of syrupy H_3PO_4 and 3 drops of I soln. (0.1%) for each 60 ml of titration mixture, or alternatively in 14 N H_2SO_4 without the addition of H_3PO_4 . Acid concn. above this value are unsuitable. In the titration of Fe^{II} with 0.05 N sodium vanadate, the indicator correction is negligible, but when using 0.01 N sodium vanadate a correction of 0.02 ml of titrant is necessary. Hydrochloric acid is not recommended as a medium for the titration of Fe^{II} because difficulties are encountered in observing the end-point. Typical results are tabulated for the titration of all three elements; I is recommended as an indicator for the standardisation of dil. soln. of sodium vanadate because of the small indicator correction required.

S. M. MARSH

23. Fractometric [gas chromatographic] determination of deuterium in a stream of hydrogen. O. Riedel and E. Uhlmann (Anal. Lab. d. Badischen Anilin- & Soda-Fabrik A.-G., Ludwigshafen a. Rhein, Germany). *Z. anal. Chem.*, 1959, **166** (6), 433-439.—Deuterium, added to H_2 gas as a tracer, is best separated on a gas chromatograph (Perkin-Elmer Fraktometer 154B) having a katharometer detector. Trials with He or Ar as carrier gas were unsuccessful, and best results were obtained with H_2 as carrier gas and a molecular sieve column (Linde 5A or Perkin-Elmer No. 1). When present,

HD behaves as if it were 0.5D₂, and is recorded as such by the instrument. The error is $\approx \pm 0.5\%$ of full-scale deflection.

T. R. ANDREW

24. Quantitative determination of sodium with α -methoxyphenylacetic acid. W. Reeve (Univ. of Maryland, College Park, U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1066-1068.—The sample soln. (containing ≈ 15 mg of Na) is treated at 25° to 30° with a 50% excess of a partly neutralised 70% aq. ethanolic soln. of α -methoxyphenylacetic acid (0.5 N in free acid, 0.3 N in tetramethylammonium α -methoxyphenylacetate). After being set aside overnight at $\approx 0^\circ$, the pptd. acid sodium salt is collected, washed with acetone, dissolved in hot H₂O, and titrated at 25° with 0.05 or 0.1 N NaOH to the phenolphthalein end-point at pH 7.8. None of the common metals interferes and the ppt. contains $\approx 97\%$ of the Na. An analysis can be made in 1 hr. if a correction is applied to compensate for the constant solubility loss. The accuracy is as high as for the zinc uranyl acetate method, and is even higher when there is more than a fourfold excess of KCl present; Li need not be removed. A two-step procedure (micro-determination of Na in the filtrate and washings) increases the accuracy to $\approx 0.04\%$.

W. J. BAKER

25. Determination of sodium in saline solutions with a glass electrode. C. A. Bower (Soil and Water Conserv. Res. Div. U.S.D.A., Riverside, Calif.). *Proc. Soil Sci. Soc. Amer.*, 1959, **23**, 29-31.—The electrode consists of a sodium aluminosilicate glass bulb filled with 0.1 N NaCl in which is immersed a silver-silver chloride electrode. A S.C.E. with a fibre-salt bridge is used for reference. The total cation content of the sample (e.g., irrigation water, soil extract) is determined by conductivity and a portion is diluted to contain ≥ 0.5 milli-equiv. of total cations and placed in a 50-ml flask. Potassium is pptd. by adding 0.1 N Ca tetraphenylboron (5 drops), the mixture is diluted to 40 to 45 ml, and brought to pH 7 (green to bromothymol blue) by the addition of 0.05 N HCl or 0.04 N Ca(OH)₂. The whole is diluted to the mark and mixed and, after 30 min., poured into a 100-ml beaker. The glass and calomel electrodes are inserted in the liquid, which is swirled, and the e.m.f. is determined at 15 to 20-min. intervals till constant. Calibration is by means of NaCl standards.

A. G. POLLARD

26. New micro-methods for the determination of potassium. N. P. Penceff (Univ. of Sofia). *Rev. Chim.*, Bucharest, 1959, **10** (4), 231-232.—The first method is based on the pptn. of K as K₂Na₂Na₂·11H₂O [Co(NO₂)₆] (I) and the polarographic determination of the Co. *Procedure*—To a soln. containing ≈ 40 μ g of K per 0.2 ml are added the reagent (45 g of Na₂[Co(NO₂)₆], 19 g of Na acetate and 18 g of acetic acid in 120 ml of H₂O), and half the vol. of 95% ethanol or water. After a few hours the ppt. is filtered off and washed on a micro filter, then re-dissolved in very dil. HCl, and evaporated to dryness. The residue is re-dissolved in 0.1 N HNO₃, and a buffer soln. of aq. NH₃-0.1 N NH₄NO₃ is added. The Co, now in the form [Co(NH₃)₆]²⁺ and [Co(NH₃)₅]³⁺, is determined polarographically by the use of the wave due to the reduction of Co³⁺ to the element. Oxygen is eliminated by addition of Na₂SO₃, and the maxima are suppressed by a few drops of methyl red. In the second method, K is pptd. as K₂[Bi(S₂O₈)₂], and the Bi is determined spectrophotometrically.

Procedure—An aliquot of a soln. containing ≈ 10 to 100 μ g of K is evaporated to dryness on a water bath. About 5 drops of the reagent are added, and after 15 to 45 min. the yellow-green ppt. is filtered off and washed 2 or 3 times with ethanol. The ppt. is re-dissolved in water and 5 ml of 2 N H₂SO₄ is added, followed by 0.2 g of KI. The orange complex (BiI₄) is then determined colorimetrically. The reagent consists of a mixture of 1 drop of Na₂S₂O₈·5H₂O soln. (10 g in 15 ml of water) and 1 drop of Bi(NO₃)₃·5H₂O soln. (4 g in 15 ml of HCl (20%)) diluted with 0.5 ml of water to which 1 drop of conc. HCl and 2 ml of ethanol (95%) have been added. The method is suitable for the determination of K in blood serum, and has a max. error of $\approx \pm 4\%$.

H. SHER

27. Separation of copper and mercury by ion-exchange chromatography. Yu. I. Usatenko and F. M. Tulyupa (F. E. Dzerzhinskii Dniepropetrovsk Chem. Tech. Inst.). *Zavod. Lab.*, 1959, **25** (4), 400-402.—Differences in the H₂SO₄ concn. at which Cu²⁺ and Hg²⁺ are completely adsorbed vary with the cationite. The greatest difference is shown by Sulpho-coal (0.25 N for Cu and 4.0 N for Hg). The normality difference for SBO is 2.75, for KU-1G, 2.5, for SPSR, 0.9, and for Wofatit R, 0.4. For the separation of Cu and Hg, a column of KU-1G treated with 1.5 N H₂SO₄ is recommended. The test soln. is passed through the column (60 ml in a 100-ml burette) at a rate of 5 ml per min. The column is then washed with 1.5 N H₂SO₄ until all the Cu is removed (0.8 to 1 litre of acid), as shown by a test with Na diethyldithiocarbamate soln. The Hg is then eluted with ≈ 300 ml of a satd. NH₄Cl soln. followed by a similar amount of dil. HCl (1:1).

G. S. SMITH

28. New application of extraction and polarographic methods. I. The determination of copper and lead in ferro-cadmium alloys. Z. Zagórski and M. Cyrankowska (Central Lab. of Accumulators and Cells, Poznań, Poland). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 495-500.—Traces of Cu and Pb are extracted from a soln. of the alloy in HNO₃ by shaking with CCl₄ in the presence of ammonium citrate buffer and Na diethyldithiocarbamate. Copper and Pb are back-extracted with dil. HNO₃ and determined polarographically.

H. DMOWSKA

29. Radiochemical evaluation of fire-assay method for determination of silver. G. H. Faye and W. R. Inman (Dept. of Mines and Tech. Surveys, Ottawa, Canada). *Anal. Chem.*, 1959, **31** (6), 1072-1076.—From radiochemical analyses with ¹¹⁰Ag as tracer, the following losses of Ag during its determination by fire-assay are reported—solubility in slag during (i) the fusion of impure lead buttons, 0.2%, and (ii) the fusion of charges giving viscous slags or of those high in sulphides of Cu or Ni or both, 2 to 3.8%; absorbed by the cupel, 2%; retained by the crucible wall, 0.5%. The total error due to these losses can amount to 5 to 10%, but with careful control it can be reduced to $\approx 3\%$. Cupellation losses vary with temp., time, size of bead and its content of Au, and the shape and composition of the cupel.

W. J. BAKER

30. Separation of silver from lead by extraction as silver isopropenylacetylde. M. Ziegler, H. Sbrzesny and O. Glemser (Anorg.-Chem. Inst., Univ., Göttingen). *Z. anal. Chem.*, 1959, **167** (2), 96-98.—

Silver can be separated from up to 45 times as much Pb by extraction of the isopropenylacetylde with dichloromethane in the presence of tributylammonium acetate. The organic layer containing all the Ag is separated and shaken with 2 N HCl, when a quant. ppt. of AgCl is obtained. This is filtered off and weighed. The aq. layer, which contains the Pb, can be titrated with EDTA (disodium salt) soln., with Eriochrome black T (C.I. Mordant Black 11) as indicator. Figures for typical separations indicate that, with 30 to 100 mg of Ag, < 98.3% is recovered. H. M.

31. New spot-test for gold. Buddhadev Sen (Coates Chem. Lab., Louisiana State Univ., Baton Rouge, U.S.A.). *Mikrochim. Acta*, 1959, (4), 513-515 (in English).—An orange-yellow chelate complex is formed between Au^{III} and phenyl α -pyridyl ketoxime. The complex is stable and is extracted from aq. soln. of pH 3 to 9 by CHCl₃. Interference is shown by platinum metals, Cu, Ni, Co, Hg^{II}, CN⁻ and organic ions such as oxalate, tartrate and citrate. Large amounts of Br⁻ and I⁻ must be absent. J. H. WATON

32. Determination of copper in beryllium metal. U.K.A.E.A. (Res. Group, Chem. Div., Chatham Outstation, Kent). AERE-AM21, 1959, 2 pp.—Details are given by J. Walkden for the method depending on the extraction of Cu as the diethylthiocarbamate complex. J. P. STERN

33. Determination of silicon in beryllium compounds (fluoride, hydroxide and ammonium fluoro-beryllate). U.K.A.E.A. (Res. Group, H.M. Gun Wharf, Chatham, Kent). AERE-AM39, 1959, 4 pp.—This method, based on that of Strickland (*J. Amer. Chem. Soc.*, 1952, **74**, 862), and written in its present form by Bowell and Heathfield, may be used for the determination of Si contents up to 2000 p.p.m. *Procedure*—Samples (0.5 g) of beryllium hydroxide are dissolved in 50% HCl, and beryllium fluoride and ammonium fluoro-beryllate in water. The soln. is treated with 5% aq. H₂BO₃, and insol. matter is filtered off, rendered soluble by fusing with Na₂CO₃, and added to the main soln. The Si in an aliquot of this soln. is converted into the reduced molybdosilicic acid complex and determined absorptiometrically. The error, which is partly due to the variable Si content of the filter-papers used in the analysis, should not exceed $\pm 10\%$ except in the lower ranges. G. S. ROBERTS

34. The simultaneous determination of calcium and magnesium. II. Colorimetric determination of traces of magnesium with Xylidyl blue II [3-hydroxy-4-o-hydroxyphenylazonaphth-2':4'-xylidide]. Hideyo Ogata and Ko Horoi (Central Res. Lab., Japan Monopoly Co-op., Yutaka-cho, Shinagawa-ku, Tokyo). *Japan Analyst*, 1959, **8** (1), 21-25.—Magnesium produces a violet chelate with Xylidyl blue II in a borax buffer of pH 9 containing 60% of ethanol. The extinction at 530 m μ is proportional to the concn. of Mg (<0.4 p.p.m.), after correction for the extinction of the reagent. There is no interference from <1600 p.p.m. of Na with 0.2 p.p.m. of Mg. The effect of Ca is related to the concn. of ethanol, but can be neglected if >15 p.p.m. of Ca is added and the concn. of ethanol is kept constant at 73%. The coeff. of variation is $\approx 2.2\%$. In the absence of Ca, the permissible lower limit of ethanol is 60%. K. SAITO

35. Photometric determination of the end-point in the complexometric titration of calcium and magnesium. E. Stengel and G. Riemer (Dortmund-Hörder Hüttenunion A.-G., Dortmund). *Z. anal. Chem.*, 1959, **167** (2), 118-120.—The Eppendorf photometer is modified by the addition of a beaker holder, which enables a beam of light to pass through the soln. being titrated. The beam passes to the photocell, and as the colour of the soln. changes the galvanometer spot moves. The holder consists of a cylinder of diam. ≈ 80 mm and depth ≈ 50 mm. Two diametrically opposed slits in the walls of the cylinder allow the light beam to pass. The titration of Ca with murexide as indicator, and of Ca plus Mg with Eriochrome black T (C.I. Mordant Black 11) can be carried out with 0.001 M EDTA to within one drop. A filter Hg578 is used, and it is not necessary to exclude stray light. H. M.

36. Amperometric determination of calcium using one or two indicator electrodes. E. Michalski and Z. Galus (Dept. of Inorg. Chem., Łódź Univ., Poland). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 431-439.—Calcium chloride in neutral soln. is titrated with K₂Fe(CN)₆ in the presence of NH₄Cl in a water-ethanol medium. The end-point is detected amperometrically (i) by using a platinum electrode as indicator, and a mercury-mercurous sulphate electrode in N H₂SO₄ as reference without an applied e.m.f., or (ii) by using two indicator electrodes and a dead-stop end-point procedure. The method can be applied to the determination of the sum of Ca and Mg in limestone. H. DMOWSKA

37. Mechanism and elimination of interferences in flame photometry. Experimental methods of investigation, and suppressing effects of aluminium, borate, phosphate and sulphate on calcium radiation. Shouzu Fukushima (Fac. of Sci., Univ. Osaka, Japan). *Mikrochim. Acta*, 1959, (4), 596-618 (in English).—The suppression of Ca radiation in the presence of BO₃³⁻, PO₄³⁻, SO₄²⁻ and Al³⁺ appears to be due to the hindering of the vaporisation process by the formation of non-volatile compounds; these are stoichiometric except that with Al. The interference diminishes when upper parts of the flame are used as the light source, and that due to BO₃³⁻, PO₄³⁻ and SO₄²⁻ is almost eliminated. Thus the interference of BO₃³⁻, PO₄³⁻ and SO₄²⁻ in the radiation of the alkaline-earth metals should be overcome by the suitable design of the photometer. J. H. WATON

38. Determination of aluminium, silicon and copper in calcium by the "single addition" method. S. Skalska and S. Held (Inst. of Gen. Chem., Warsaw, Poland). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 543-548.—The method is applied to the determination of Al, Si and Cu in calcium [after its conversion into Ca(OH)₂] in concn. of 5 to 50 μ g per g of Ca(OH)₂. H. DMOWSKA

39. Determination of calcium oxide and silica in lead melting slags. A. N. Karolev and R. A. Karanov (Lead-Zinc Works, Kirjali, Bulgaria). *Zavod. Lab.*, 1959, **25** (4), 413-415.—The sample (0.2 g) is dissolved in 5 ml of HF and 2 ml of HNO₃ for the determination of CaO. The soln. is evaporated to dryness, and the treatment with acid and evaporation is repeated twice, and a final evaporation is carried out with 5 ml of HNO₃. The dry residue is dissolved in 10 ml of dil. HNO₃ (1:1), the soln. is diluted with hot water (150 to 200 ml) and

boiled, 0.1 to 0.2 g of EDTA (disodium salt) is added (as a 4% soln.) to form a complex with Pb, and then the soln. is treated with a few drops of methyl red indicator soln. and 50 ml of hot 5% ammonium oxalate soln., and neutralised with aq. NH_3 . The soln. is boiled for 1 to 2 min. and set aside for 20 to 25 min. at 80° to 90° . The ppt is collected and washed with cold water containing aq. NH_3 , then dissolved in dil. H_2SO_4 and titrated with 0.05 N KMnO_4 . For the determination of SiO_2 , a 0.1-g sample is fused in a silver crucible with 3 g of Na_2O_2 and 1 g of NaOH , and a modification of the molybdenum blue colorimetric method is applied to the soln. of the melt in acid.

G. S. SMITH

40. Determination of beryllium in aluminium alloys by means of beryllon II. L. M. Budanova and B. A. Zhukova. *Zavod. Lab.*, 1959, **25** (4), 411-413. —The sample (1 g) is dissolved in the cold in 50 ml of 20% NaOH soln. and the whole is diluted to 250 ml. A suitable aliquot of the filtered soln. (25 ml for contents between 0.001 and 0.01%, 5 ml for contents between 0.01 and 0.1%) is neutralised with dil. HCl (1:1) and 20% NaOH soln. so that there are 2 to 3 drops of NaOH soln. in excess, and then treated with 20 ml of 0.5% NaOH soln. and 5 ml of a 0.02% aq. soln. of beryllon II (cf. Lukin and Zavarikhina, *Anal. Abstr.*, 1957, **4**, 1447), followed by dilution to 100 ml. The extinction with a red or orange filter is measured after 10 min., and the content is found by use of a calibration curve. With slight modifications the method can be applied to alloys containing several per cent. of Be. No interferences are reported.

G. S. SMITH

41. Studies in qualitative inorganic analysis. XII. Comparison of the methods used in the group separation of strontium and calcium ions. W. F. Jones (Sci. Dept., Victoria Inst., Worcester, England). *Mikrochim. Acta*, 1959, (4), 635-639 (in English). —Potassium chromate in the presence of aq. NH_3 and ethanol is recommended as a suitable reagent for the separation of Sr and Ca. *Procedure* —After the removal of Ba by the addition of 10 drops of 5% K_2CrO_4 soln., the vol. is reduced to ≈ 1 ml. Then 3 drops of 4 N aq. NH_3 , 5 drops of K_2CrO_4 soln. and 0.5 ml of ethanol are added, and the soln. is boiled and set aside for 5 min.; the ppt. of SrCrO_4 is removed by centrifuging. The soln., free from Sr, is boiled to remove ethanol and is diluted with an equal vol. of H_2O ; 3 drops of 4 N chloroacetic acid and 2 drops of satd. ammonium oxalate soln. are added. The soln. is warmed and set aside for 5 min. A white ppt. indicates Ca.

J. H. WATON

42. Spectrographic determination of strontium in the ash of bone, milk and vegetation. U.K.A.E.A. (Res. Group, Chem. Div., Woolwich Outstation, Royal Arsenal, London). AERE-AM15, 1959, 5 pp. —Details of a method based on that of Hodges *et al.* (*J. Biol. Chem.*, 1950, **185**, 519) and of Jury *et al.* (A.E.R.E. Report C/R 2614) are given. The procedure is written in its present form by Webb.

J. P. STERN

43. Detection of barium and strontium in the insoluble sulphates. P. Luis (Univ. Nacional, Buenos Aires). *Mikrochim. Acta*, 1959, (4), 536-540 (in English). —The sulphates (0.5 mg), which must not contain PbSO_4 , are twice evaporated to dryness with 25 to 30 μl of 12.5% KI and 75 μl of

60% HClO_4 . An extract of the perchlorates of Ba and Sr in 70 μl of acetone is separated with a capillary pipette and is used for the rhodizone test on filter-paper. The red spot so produced is treated with several small drops of oxalate reagent (5 ml of conc. aq. NH_3 added to 100 ml of satd. Na oxalate soln.). The persistence of the red spot indicates the presence of Ba with perhaps some Sr; the fading of the colour indicates the presence of Sr with perhaps some Ba. In testing for the minor component, three more extracts with 50 to 70 μl of acetone are evaporated to dryness in a centrifuge cone and the residue is dissolved in 50 to 70 μl of H_2O . Then 10 to 15 μl of chromate reagent (4 g of CrO_3 and 12 g of neutral ammonium acetate in 100 ml of H_2O) is added, and 2 to 3 min. later the soln. is centrifuged. A ppt. will be given by 1 μg of Ba in the presence of 250 μg of Sr. To detect Sr, the chromate soln. is treated with 20 to 25 μl of ammonium carbonate reagent (satd. soln. in 4 M aq. NH_3) and 50 μl of acetone. After a few minutes the soln. is centrifuged; a white ppt. indicates Sr (or perhaps Ca). To confirm Sr, the ppt. is dissolved in 50 μl of 0.1 M acetic acid, evaporated to dryness with HClO_4 and extracted with 50 μl of acetone. The rhodizone test is repeated, and if necessary the spot obtained is compared with a blank prepared from 50 μl of 1% BaCl_2 soln. free from Sr. In this way, 1.25 μg of Sr may be detected in the presence of 250 μg of Ba.

J. H. WATON

44. Separation of radium and barium by ion-exchange elution. W. H. Power, H. W. Kirby, W. C. McCluggage, G. D. Nelson and J. H. Payne, jun. (Mound Lab., Monsanto Chem. Co., Miamisburg, Ohio, U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1077-1079. —Radium can be separated from Ba-Ra mixtures (in ratios as high as 4440:1) by adding the sample soln. to a 25-cm column of cation-exchange resin (Dowex 50, NH_4^+ form, 50 to 100 mesh). On eluting with 0.32 M ammonium citrate at pH 5.6 and $\approx 25^\circ$, Ba is eluted between 6 and 18 column-vol. (peak at 10 vol.) and Ra between 21 and 39 vol. (peak at 31 vol.). In a separation of 158 mg of Ba and 1.8 mg of Ra, 99% of the Ra was recovered with a content of Ba of $\approx 0.1\%$. Conditions affecting the pptn. of slightly sol. barium citrate during the elution are discussed.

W. J. BAKER

45. Quantitative spectrochemical analysis of refined zinc. O. Werner (Bundesanst. Materialprüfung, Berlin-Dahlem, Germany). *Metall*, 1958, **12**, 697-707. —Specimens of refined zinc with varied contents of Cd and Sn (0.002 to 0.06%), and samples containing between 0.25 and 3.0% of Pb were studied, and the effect of the Pb content on the determination of Sn and Cd was studied. It was found that the Cd determination was not influenced by the Pb present, but Sn in concn. above 0.01% was affected by as little as 0.25% of Pb, the intensity of the Sn lines being greatly increased. Overheating the melt also affected the determination of Sn but not that of Cd. By auto-radiographic and metallographic studies it was found that Sn was localised in the heterogeneous lead structure, while Cd was found in the zinc, whether the sample was poor or rich in Pb. On this basis the Pb present was without influence on the excitation of Cd so long as an equilibrium displacement had not been produced by overheating the melt. The method of excitation is not important for this work. A d.c. arc can be used in place of the a.c. arc.

CHEM. ABSTR.

46. (2-Hydroxy-5-methoxyphenylazo)-4-methylthiazole as an analytical reagent. III. Determination of zinc. Tadashi Yanagihara, Nobuhisa Matano and Akira Kawase (National Res. Lab. for Metals, Nakameguro, Meguro-ku, Tokyo). *Japan Analyst*, 1959, 8 (1), 10-14.—This reagent produces a water-soluble 1:1 chelate (max. absorption 594 $m\mu$) with Zn in weakly acid soln. and a 1:2 (Zn to reagent) chelate in weakly alkaline soln. The latter chelate, which is slightly soluble in water, is extracted with isoamyl alcohol at pH 9.0 and gives max. absorption at 612 $m\mu$, the extinction being proportional to the amount of Zn (< 10 μg per 10 ml of isoamyl alcohol). This reagent can also be used as an indicator for the back-titration of Zn at pH 9.0 in the presence of an excess of EDTA (colour change, purple to blue).

IV. Determination of nickel and cobalt. Tadashi Yanagihara, Nobuhisa Matano and Akira Kawase. *Ibid.*, 1959, 8 (1), 14-17.—This reagent gives blue chelates with Co and with Ni at pH 7 to 9 in a molar ratio of 1:2 (metal to reagent). The chelates are insoluble in water and extractable with isoamyl alcohol, giving max. absorptions at 620 $m\mu$ (for Ni) and 607 $m\mu$ (for Co). Each metal (< 10 μg) is extracted from an aq. soln. at pH 8.0 and determined colorimetrically. K. SAITO

47. Metallurgical polarographic analysis. VIII. Rapid determination of zinc in iron ores in the presence of nickel and cobalt. Yoshiaki Miura (Tech. Res. Inst., Yamata Iron and Steel Works, Fukuoka-ken). *Japan Analyst*, 1959, 8 (1), 5-9.—In a supporting electrolyte containing *M* acetic acid, *M* ammonium acetate, 0.03 *M* NaSCN and 0.003% of gelatin, Zn gives a well-defined wave at -1.05 V *vs.* the S.C.E., whereas the E_1 for Ni is -0.74 V, and Co^{II} gives no wave before -1.2 V. The wave height for Zn (< 5 mg per 50 ml) is proportional to the concn. Tervalent Cr (-1.07 V), Mo (-0.53 V), V (-1.20 V) and Ti (-0.83 V, -1.33 V) also give reduction waves, but are less common in iron ores. The amount of Fe must be decreased to < 50 mg per mg of Zn by extraction with diethyl ether. Procedure—Dissolve the sample (0.5 g) in HCl (1:1) (10 ml) and a small amount of HNO_3 and heat with further addition of HCl (1:1) (10 ml). Extract most of the Fe with ether and evaporate the aq. layer to dryness. Dissolve the residue in HCl (1:1) (5 ml) and make up to 100 ml with the required amounts of the salts mentioned above. Mix a 5-ml aliquot with gelatin and record the polarogram. K. SAITO

48. Complexometric determination of mercury in mercury compounds. I. R. Přibil and E. Kőrös (Czech. Acad. Sci., Prague). *Acta Pharm. Hung.*, 1957, 27, 1-4.—The sample soln. containing Hg^{2+} is buffered with hexamine (I) to pH 5 to 6 and the Hg in micro or macro amount is titrated complexometrically, in the presence of Xylenol orange. Interference by halogens can be eliminated by a preliminary pptn. with $AgNO_3$. Dilute the soln. (containing 0.01 to 1 mg of Hg^{2+}) to 20 to 100 ml and add a 20% soln. of I until a red-violet colour appears. Add 4 to 6 drops of 0.1% Xylenol orange and titrate the soln. with 0.05 *M* EDTA to a yellow colour (1 ml of 0.05 *M* EDTA = 10.03 mg of Hg).

II. Assay of inorganic mercury compounds. R. Přibil, E. Kőrös and L. Barcza. *Ibid.*, 1957, 27, 145-151.—A complexometric procedure for the determination of the Hg content of metallic mercury, aminomercuric chloride, HgI_2 , Hg_2Cl_2 , mercuric oxycyanide, $Hg(CN)_2$, and HgS was developed.

The method is based on the titration of Hg^{2+} , at pH 4.5 to 6, in the presence of Xylenol orange, with a complexing agent. The accuracy of the procedure is reported to be within $\pm 0.1\%$.

III. Assay of organic mercury compounds. R. Přibil, E. Kőrös and L. Barcza. *Ibid.*, 1957, 27, 243-245.—Titration at pH 4.5 to 6 after complete destruction of the sample gives exact results even with compounds containing N. For N-free mercury compounds, heat 0.20 g with 2 ml of H_2SO_4 and twice with 2 ml of H_2O_2 ; cool and dilute to 100 ml. Dilute 10 ml of this soln. to 50 ml and titrate with EDTA, with 5 to 6 drops of Xylenol orange as indicator; to the yellow soln. add 10% NaOH soln. dropwise until faintly violet, re-acidify quickly with a few drops of HNO_3 until again yellow, adding 3 to 4 drops in excess and 1 to 2 ml of 20% hexamine soln. Titrate the violet-red soln. with 0.05 *M* EDTA to a yellow end-point. For N-containing mercury compounds, treat a 0.1-g sample with 3 to 4 ml of HNO_3 , evaporate to 1 ml, and treat 3 times with 2 ml of H_2O_2 and with 2 ml of HNO_3 ; reduce to 1 ml, cool, and dilute to 100 ml. Mix 20 ml of this soln. with 10 to 15 ml of 20% hexamine soln. and 30 ml of water and titrate with EDTA, with Xylenol orange, as before. The end-point of the 0.005 *M* EDTA titration is the change from violet-red to yellow. CHEM. ABSTR.

49. Colorimetric determination of boron with Victoria violet. C. A. Reynolds (Dept. of Chem., Univ. of Kansas, Lawrence, U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1102-1104.—From 0.02 to 0.60 mg of B can be determined spectrophotometrically by measuring the extinction at 540 $m\mu$ of the coloured complex formed, after ≈ 30 min., between H_3BO_3 and Victoria violet (C.I. Acid Violet 3) (0.5×10^{-3} *M*) at pH 8.75 \pm 0.05 (carbonate buffer). The height of the differential extinction peak (*i.e.*, against the blank) is compared with a calibration graph which is rectilinear in the range 25 to 550 μg of B per 25 ml. The accuracy is within 0.01%. Strong oxidising agents and cations that react with chromotropic acid or its derivatives must be absent. W. J. BAKER

50. Studies in qualitative inorganic analysis. IX. Detection of aluminium ion. W. F. Jones (Sci. Dept., Victoria Inst., Worcester, England). *Mikrochim. Acta*, 1959, (4), 544-546 (in English).—A 0.1% aq. soln. of Solochrome cyanine (C.I. Mordant Blue 3) is preferred to aluminon for the confirmation of Al in qual. analysis. The reagent is sensitive to very small amounts of Al and is less sensitive to Fe^{III} and Cr^{III} than is aluminon. In the recommended procedure for the group separation, the $Al(OH)_3$ in the group ppt. is dissolved in a few drops each of 4 *N* NaOH and 20-*vol.* H_2O_2 . After boiling and separating, 2 drops of this soln. are added to 2 drops of reagent in 4 drops of 50% ammonium acetate soln. A reddish-purple colour or ppt. indicates the presence of Al. J. H. WATON

51. Determination of aluminium as sodium fluoroaluminate. H. W. Pender (Chase Brass and Copper Co., Waterbury, Conn., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1107-1109.—The rapid gravimetric procedure described is applicable to alloys of titanium, copper, zinc or manganese containing from 1 to 10% of Al. No initial separation of other metals is required and the precision and accuracy equal those of the longer methods. The sample is dissolved in dil. HF, the soln. is oxidised with H_2O_2 .

and the Al is then pptd. at 25° by the addition of a 2% soln. of NaF. The centrifuged ppt. is washed into the original beaker with water, and the mixture is boiled, re-pptd. and centrifuged as before. After being washed with 0.5% aq. NaF soln. and drying for 1 hr. at 125° to 130°, the ppt. is weighed as $11\text{NaF} \cdot 4\text{AlF}_3$. This formula is confirmed by chemical and X-ray diffraction analyses, and represents the compound formed when the concn. of NaF in the soln. is <1.4%. W. J. BAKER

52. Determination of oxygen in aluminium by means of vacuum fusion. L. Kopa (Res. Inst. Ores, Panenské Břežany, Czechoslovakia). *Hutn. Listy*, 1959, **14** (4), 322-324.—The vacuum-fusion method of Sloman (*Brit. Abstr. C*, 1946, 77) has been tested for the determination of O in aluminium, and some disadvantages have been eliminated by replacing the steel bath with a copper bath, and by using a temp. of 1550°. The apparatus consists of a high-frequency furnace, diffusion pump, Toepler pump, analyser for the extracted gases and single-stage rotary oil-pump. J. ZYKA

53. Fluorimetric determination of gallium in metallic germanium. Tsunenobu Shigematsu (Inst. for Chem. Res., Kyoto Univ., Sakyo-ku). *Japan Analyst*, 1958, **7** (12), 787-788.—Since Ge (<80 mg) does not interfere with the fluorimetric determination of Ga with 8-hydroxy-2-methylquinoline (I) (Ishibashi *et al.*, *Anal. Abstr.*, 1958, **5**, 2140) this method was applied to the rapid (≈ 30 min.) determination of Ga (0.1 to 100 p.p.m.) in metallic germanium. The error is <0.05 μg for 0.1 to 5 μg of Ga. *Procedure*—Dissolve the sample (0.1 to 1 g) in NaOH soln. (2 to 4 g in 20 ml) and H_2O_2 (30%, 5 to 10 ml), make acid with HCl and dilute to 100 ml. Dilute an aliquot (10 to 30 ml) to 40 ml, add I (1% in *N* acetic acid, 1 ml) and ammonium acetate soln. (20%, 5 ml), adjust the pH to 3-9 with *N* HCl and extract with freshly distilled CHCl_3 (3 \times 10 ml). Dilute the CHCl_3 layer to 50 ml, dry with Na_2SO_4 and measure the fluorescence at 540 $\text{m}\mu$, with fluorescein sodium soln. (0.16 μg per ml) as standard. K. SAITO

54. Spectral determination of indium, thallium and gallium. N. M. Krasnobaeva. *Khim. i Ind., Sofia*, 1958, **30** (1), 17-18.—The lines used were 4101-773 and 4511-323 (In), 4172-056 (Ga), and 3775-72 and 3519-24 \AA (Tl). If the material to be analysed was mixed with a powder consisting of K_2SO_4 - ZnS (1:1), a background was created which allowed a clear recognition of the lines; a linear dependency of the intensity change was then found in the region from 0.005 to 0.008% of Tl, In or Ga. CHEM. ABSTR.

55. Detection and determination of thallium with methyl violet. M. Kovarik and M. Moučka (Inst. for Anal. Chem., Coll. of Mining, Ostrava, Czechoslovakia). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 615-618 (in German).—A 0.2% aq. soln. of methyl violet gives a benzene-soluble blue complex with Tl^{III} in HCl soln. *Procedure*—A drop of test soln. is treated with a drop of saturated bromine water, and the excess of Br is destroyed with a crystal of sulphosalicylic acid. Then two drops of conc. HCl and two drops of reagent are added. The soln. is shaken with ≈ 0.2 ml of benzene; a blue colour in the organic layer indicates Tl. The interference shown by Hg, Au and Sb is overcome by reducing with metallic copper. The blue colours given by Mo^{VI} , W^{VI} and V^{V} are not extracted by

benzene. For the quant. determination, Tl^{III} is oxidised with bromine water and the excess of bromine is destroyed with sulphosalicylic acid. An equal vol. of HCl (1:1) is added, and then twice the vol. of 30% sodium citrate soln. After the addition of 1 ml of 0.2% methyl violet soln., the blue-green complex is extracted by shaking three times with 10 to 20 ml of benzene. The combined extracts are diluted to 100 ml with benzene and the extinction is measured at 610 $\text{m}\mu$. The Beer - Lambert law is obeyed for up to 180 mg of Tl in 100 ml of benzene. J. H. WATON

56. Analytical chemistry of thallium. I. Complexometric determination. A. I. Busev and V. G. Tiptsova (M. V. Lomonosov State Univ., Moscow). *Zhur. Anal. Khim.*, 1958, **13**, 180-185.—Tervalent Tl was titrated amperometrically with EDTA (disodium salt) at pH 1 to 2 with 1-(2-pyridylazo)-2-naphthol as indicator. Iron, Bi and Cu interfere, as do the oxidising ions MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and $\text{S}_2\text{O}_8^{2-}$; Zn, Cd and Pb do not interfere.

II. Precipitation of tervalent thallium bromide complexes with some pyrazolone derivatives. A. I. Busev and V. G. Tiptsova. *Ibid.*, 1959, **14** (1), 28-36.—In the presence of Br^- , Tl^{3+} are pptd. by phenazone, amidopyrine, diantipyrylmethane (I) and diantipyrylphenylmethane, giving, respectively, a white ppt. turning greenish-yellow [$(\text{C}_{11}\text{H}_9\text{ON}_3)_3\text{TlBr}_4$]; a yellowish-white ppt. [$(\text{C}_{11}\text{H}_9\text{ON}_3)_2\text{TlBr}_3$]; a ppt. resembling AgBr [$(\text{C}_{11}\text{H}_9\text{ON}_3)_2\text{TlBr}_2$]; and a lemon-yellow ppt. [$(\text{C}_{11}\text{H}_9\text{ON}_3)_2\text{CHCl}_2\text{TlBr}_2$]. Only the compound formed with I is suitable for the determination of Tl. For the gravimetric determination, to an acid soln. of $\text{Tl}(\text{NO}_3)_3$ or $\text{Tl}_2(\text{SO}_4)_3$ add a 1% soln. of I and 1 to 2 ml of HBr for each 5 mg of Tl, filter off the ppt., wash it with 1% HBr soln. and dry it at 100° to 120° to const. wt. Zinc, Cu and Cd do not interfere; procedures are described for complexing Fe and Bi with EDTA (disodium salt). With a ratio of Fe to Tl > 10:1, re-pptn. may be necessary. Antimony is complexed with tartaric acid. In determining 6-40 to 45.7 mg of Tl (alone or in the presence of Zn, Cd, Cu, Bi, Sb or Fe) the max. error was 0.6 mg. I may be used to determine Tl amperometrically; the determination of Tl (0.52 to 1.31 mg in KBr soln. of various concn.) had a max. error of 4.0%. CHEM. ABSTR.

C. D. KOPKIN

57. Complexometric determination of thallium, lanthanum and cerium(III) with carminic acid. J. Dobrowolski (Dept. of Gen. Chem., Med. Coll., Szczecin, Poland). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 609-614.—Thallium, Ce and La are determined by complexometric titration with EDTA (disodium salt) in a soln. buffered to pH 3.7, with carminic acid as indicator. The titration is carried out hot. The colour change is from violet to yellow. H. DMOWSKA

58. Amperometric titration of thallium without applied e.m.f. E. Michalski and W. Stapor (Dept. of Inorg. Chem., Łódź Univ., Poland). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 441-444.—Thallium as TlNO_3 or Tl_2SO_4 is titrated amperometrically in 20% ethanol soln. with 0.1 *N* KI, by using (i) a rotating platinum electrode or (ii) a stationary indicator electrode, in each case with a calomel reference electrode with KNO_3 in place of KCl; the former method gives better results. The error of determination is >0.1%; the smallest amount of Tl determined was 40 mg. H. DMOWSKA

59. Micro-volumetric chromatographic method of determining individual rare-earth elements in mixtures. R. S. Lauér and N. S. Poluéktov (Inst. of Gen. and Inorg. Chem., Acad. Sci., UkrSSR). *Zavod. Lab.*, 1959, 25 (4), 391-396.—The method is based on paper chromatography of the thiocyanates and complexometric determination of the elements in the localised zones. The sample (20 to 30 mg) of mixed oxides is dissolved in 0.5 to 1 ml of conc. HCl, the soln. is evaporated to dryness and the residue is dissolved in 0.05 ml of 0.3 N HNO₃. A drop ($\approx 1 \mu$ l) is placed on a marked position 15 to 17 cm from one end of a strip of filter-paper (2 cm \times 45 cm) which has been soaked in 10% NH₄NO₃ soln. and dried. To obtain several chromatograms simultaneously, a wider paper (10 cm \times 50 cm), with drops placed 2.5 to 3 cm apart, can be used. The paper is dried in air and placed for 30 to 40 min. in a jar containing wadding moistened with NH₄NO₃ soln. It is then placed in a cylinder containing 30 ml of a solvent prepared by mixing 30 ml of a mixture of acetone and diethyl ether (1:1) with a soln. of 0.25 g of NH₄SCN in 0.4 ml of water, then adding 0.3 ml of concn. HCl and filtering from the pptd. NH₄Cl. After 4 to 6 hr. the paper is removed and dried, then moistened along its length with a 0.35% ethanolic soln. of alizarin containing 3% of hexamine to develop the rare-earth-element zones as blue patches on a yellow background. Identification of the individual elements is made by reference to a standard soln. on a similar chromatogram. The strip is cut up and the individual zones are boiled with 2 ml (or 1 ml) of 0.0005 M EDTA (disodium salt), with the addition of 1 drop of 0.5 N HCl if the blue colour is not discharged. Each soln. is mixed with 2 ml of water, 0.3 ml of a 40% aq. soln. of hexamine, 0.1 ml of 5% Na salicylate soln. and 0.1 ml of a 0.1% aq. soln. of arsenazo (as indicator), and then titrated with LaCl₃ soln. until the colour changes from pink to reddish blue. The titrant is prepared by diluting to 100 ml 5 ml of a stock soln. obtained by moistening 0.1000 g of freshly ignited La₂O₃ with water, dissolving in 0.5 ml of HCl, evaporating to dryness, dissolving the residue in water with the addition of 1 ml of concn. HCl, and diluting to 100 ml. The amount of LaCl₃ soln. required to titrate 2 ml of the EDTA soln. is determined, and appropriate factors are used to calculate the contents of the individual rare-earth elements. The method was tested on mixtures containing La, Pr, Nd, Sm and Y. G. S. SMITH

60. Photometric determination of cerium with o-tolidine. N. Jordanov and C. Daiev (Lehrstuhl f. Anal. Chem., Univ., Sofia). *Compt. Rend. Acad. Bulg. Sci.*, 1959, 12 (2), 149-152 (in German).—Cerium (up to 300 μ g) is co-pptd. with La as the oxalate. The ppt. is set aside for 24 hr., filtered off and ignited at 800° to 900°. The residue is dissolved in hot conc. H₂SO₄ (10 to 12 drops), o-tolidine soln. (0.05% in 10% H₂SO₄) (1 ml) is added and after diluting the soln. to 100 ml the extinction is measured at 410 m μ . The colour is stable for 12 min. and is unaffected by pH in the range 0 to 4. Thorium and the rare-earth metals do not interfere, but Fe, Ti and Mn do. W. T. CARTER

61. Carrier-free separation of lanthanum-140 from barium-140 by the leaching-out method. Nagao Ikeda and Hiroshi Ebihara (Fac. of Sci., Tokyo Univ. of Education, Koishiwaka). *Japan Analyst.*, 1959, 8 (1), 39-42.—The leaching-out of ¹⁴⁰La from ¹⁴⁰BaSO₄ was examined with HCl of various concn. The BaSO₄ is pptd. from the soln.

containing ¹⁴⁰La and ¹⁴⁰Ba, with BaCl₂ as carrier, by Heyn and Schupak's method of homogeneous pptn. (*Anal. Chem.*, 1954, 26, 1243). The elution of La and of ¹⁴⁰Ba increases with increase in concn. of HCl (up to 2 N); the leaching-out of ¹⁴⁰Ba is decreased by the addition of ethanol. By the use of a mixture of 3 N HCl and ethanol (1:1), the radiochemical purity of the extracted ¹⁴⁰La is $\approx 99\%$. K. SAITO

62. Controlled-potential coulometric determination of europium. W. D. Shults (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1095-1098.—In the rapid and accurate procedure described, 1 ml (≈ 5 to 10 mg of Eu) of the sample soln. (EuCl₃ in 0.05 to 1 M HCl) is electrolysed at a mercury cathode and a controlled potential of -0.8 V (vs. a silver-silver chloride electrode). The Eu³⁺ are then oxidised to Eu²⁺ with 100% current-efficiency at a silver-silver chloride electrode with the potential controlled at -0.1 V, the read-out voltage (V) being measured when the current falls to 50 μ A. In both electrolyses pure N is passed through the soln. The wt. of Eu titrated is given by (V \times 62.59) mg. Rare-earth elements and other impurities in commercial Eu₂O₃ do not interfere. The apparatus used is that described by Shults and Thomason (*ibid.*, 1959, 31, 492). W. J. BAKER

63. Separation of lanthanides from mixtures of their chlorides. J. H. Freeman (A.E.R.E., Harwell, Berks., England). *J. Inorg. Nuclear Chem.*, 1958, 7 (3), 286-287.—A mixture of Nd₂O₃ (1 g) and Dy₂O₃ (1 g), dissolved in HCl, was dehydrated with thionyl chloride and the anhydrous chlorides were then shaken with acetone (20 ml); it was found that the ratio of Nd to Dy in soln. was 24 to 76. In a similar experiment with Dy₂O₃ and Gd₂O₃, the ratio of Gd to Dy in soln. was 35 to 65. After about 66% conversion to the anhydrous state of a mixture of NdCl₃ and DyCl₃, it was heated in a stream of A and then leached with H₂O; the ratio of Nd to Dy in soln. was 70 to 30. In a similar experiment with DyCl₃ and GdCl₃, the ratio of Gd to Dy in soln. was 54 to 46. G. J. HUNTER

64. Ion-exchange studies of the actinide elements. G. R. Chopin (Florida State Univ., Tallahassee). *J. Chem. Educ.*, 1959, 36 (9), 462-465.—A review with 26 references.

65. Spectrophotometric titration of parts per million of carbon dioxide in gases. J. W. Loveland, R. W. Adams, H. H. King, jun., F. A. Nowak and L. J. Cali (Res. and Engng Dept., Sun Oil Co., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1008-1010.—The CO₂ is absorbed in dil. NaOH soln. and the excess of alkali is back-titrated with dil. HCl, the titration being followed spectrophotometrically at 555 m μ , with phenolphthalein as indicator. A special absorption bulb is used and gives a complete recovery of all CO₂ up to flow rates of 100 ml per min. The sensitivity is ≈ 1 p.p.m. of CO₂ for 20 litres of gas. In the range from 1 to 10 p.p.m. the accuracy is ≈ 1 p.p.m. and the standard deviation is $\approx \pm 0.4$ p.p.m. Other acidic gases interfere. K. A. PROCTOR

66. Determination of quartz in sulphide ores [of non-ferrous metals]. M. N. Fedorova and Yu. V. Klimenko. *Trudy Nauch. Proekt. Inst. "Ural-mekhanobr."*, 1958, (3), 150-154; *Ref. Zhur., Khim.*,

1959, (4), Abstr. No. 11,496.—*Procedure*—Calcine the test sample, treat the ash with cold dil. HNO_3 in the presence of KClO_4 , boil with HCl (to eliminate elementary S, add a second portion of KClO_4 and boil again), dilute the supernatant liquid with H_2O , shake, allow the ppt. to settle and then decant (repeat the dilution and decanting). Add HCl and 3% NaF soln. to the insol. residue (chlorite-sericite schist) and heat at 90° to 95° for 8 hr. Dilute the liquid obtained with H_2O , allow the residue to settle and siphon off the liquid as completely as possible. Neutralise the remaining supernatant liquid and heat with 10% KOH soln. at 90° to 95° for 2 hr., dilute with H_2O and filter. Wash the ppt. with H_2O , then with dil. acid and again with H_2O , ignite in a platinum crucible and determine the SiO_2 in the usual way. The relative error of the determination is $\approx 4\%$. A method is also described for the determination of quartz inclusions in sulphide ores; the sample (100 to 250 g) is decomposed as described above, but the calcination is not carried out before the treatment with acids but after the decomposition of the sulphides; the treatments with HCl and NaF , and with KOH , are carried out twice. K. R. C.

67. Use of an impulse source for spectra excitation in the analysis of silicates. V. V. Korolev and E. E. Vainshtein (V. I. Vernadskii Inst. Geochem. and Anal. Chem. Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1958, 13 (6), 627-634.—A d.c. carbon arc was augmented by an impulse source, a condensed spark fed from a generator. The conditions were: min. inductance; capacitance 0.02 microfarad; discharge gap 0.5 to 3 mm. A more uniform distribution of excited atoms and ions in the plasma is produced as compared with the d.c. arc. In the method developed for the quant. determination of Si, Ti, Al, Fe, Ca, Mg, Mn, Na and K in silicate rocks there is no necessity for dilution with CuO or carbon. The mean error of each determination is 2 to 3% and the difference between spectrographic and chemical analyses does not exceed 4%.

W. Roubo

68. Determination of germanium after extraction by isobutyl methyl ketone. II. P. Senise and L. Sant'Agostino (Dept. de Quím., Fac. de Filos., Ciênc. e Letr., Univ., São Paulo, Brasil). *Mikrochim. Acta*, 1959, (4), 572-581 (in English).—After extraction from HCl soln. with isobutyl methyl ketone (I) (cf. *Anal. Abstr.*, 1956, 3, 3589), Ge is determined spectrophotometrically in the organic phase with phenylfluorone (II). *Procedure*—The sample soln. (1.0 ml) containing 0.8 to 2.5 μg of Ge and $\approx 3.5 N$ in H_2SO_4 is shaken with 0.1 ml of satd. aq. cupferron soln. and 0.5 ml of I to remove interfering ions. The extraction is repeated with 3 or 4 more 0.5-ml additions of I. Then the aq. soln. is acidified with 2.0 ml of conc. HCl and is shaken with 1.0 ml of I to extract the Ge. The extraction with I is repeated (2×0.7 ml). To the combined organic layers is added 3 ml of reagent soln. (0.050 g of II dissolved in 200 ml of ethanol containing 12.5 ml of H_2SO_4 and diluted to 250 ml with ethanol), and the soln. is diluted to 10 ml with ethanol. The extinction of the soln. is measured at 504 $m\mu$ against a reagent blank. Calibration curves are prepared by the same procedure. In the presence of WVI , 0.2 ml of 60% NH_4SCN soln. is added to the sample soln., which is then reduced by heating on a water bath at 70° to 75° for 10 min. with 0.1 ml of a satd. aq. soln. of ascorbic acid. When cool, the soln. is extracted with 0.5 ml of I,

and the excess of SCN^- is removed by further extractions with I (5×0.5 ml). In the presence of NbV , the procedure resembles that for WVI , but after the first extraction a further 0.2 ml of NH_4SCN soln. is added. After further heating and cooling, the soln. is extracted ten times with 0.5-ml portions of I. The standard deviation of the extinction at the 0.8- μg level is 0.0022 and at the 2.0- μg level is 0.0025 (20 determinations). The procedure is suitable for the determination of Ge in coal.

J. H. WATON

69. Absorptiometric determination of germanium with phenylfluorone. F. H. Kunstmann and E. F. E. Müller (Fuel Res. Inst. of S. Africa, P.O. Box No. 217, Pretoria). *Analyst*, 1959, 84, 324-325.—The absorptiometric method of Cluley (*Analyst*, 1951, 76, 523) gives high results in the presence of Cl, which intensifies the colour of phenylfluorone soln. Not only must no substance capable of oxidising HCl be present when Ge is distilled from fairly conc. HCl , but such oxidising substances must not be formed in the initial stages of the procedure. Experiments described showed that the high results obtained for the Ge content of some coals were due to the presence of Mn. The addition of FeSO_4 or Na oxalate before distillation prevented the formation of manganese compounds of higher valency, and correct results were then obtained. Since FeSO_4 has the advantage of reducing Cl, as well as compounds of Mn and V, the use of Na oxalate was abandoned. A. O. JONES

70. Spectrophotometric determination of germanium with phenylfluorone. J. D. Burton and J. P. Riley (Oceanography Dept., Univ., Liverpool, England). *Mikrochim. Acta*, 1959, (4), 586-591 (in English).—The procedure described by Cluley (cf. *Analyst*, 1951, 76, 523) has been modified with the object both of reducing the high reagent blank and removing the interference of other elements. A H_2SO_4 medium replaces one of HCl , and smaller amounts of phenylfluorone and acacia gum are used. Beer's law applies over the range 0.1 to 0.6 p.p.m. of Ge; for the determination of lower concn., 0.05 p.p.m. of Ge is added to both sample and blank. The addition of EDTA (disodium salt) suppresses the interference of commensurate amounts of As, Ga, In, Te, Tl and Sn, and of an excess of Fe. The interference of Sb is not completely eliminated in this way, and the addition of 1 ml of 1% citric acid soln. is recommended. *Procedure*—To the test soln. are added 5 ml of 14.3% H_2SO_4 , 1 ml of aq. EDTA (disodium salt) soln. (0.5%), 6 ml of ethanol, 1 ml of acacia gum soln. (0.1 g in ≈ 80 ml of boiling H_2O , filtered and diluted to 100 ml) and 1.5 ml of phenylfluorone reagent (0.05 g of phenylfluorone dissolved in 75 ml of ethanol and 5 ml of 14.3% H_2SO_4 , and diluted to 100 ml with ethanol). The soln. is diluted to 25 ml with H_2O , and after 2 hr. the extinction is measured at 520 $m\mu$ against a reagent blank.

J. H. WATON

71. Photometric determination of tin in zinc and lead. E. Eberius (Lab. A.-G. Zinkind., Duisburg-Hamborn, Germany). *Metall.*, 1958, 12, 721-724.—For zinc and zinc alloys the sample is dissolved in HCl (sp. gr. 1.08). Any residue is dissolved by the addition of H_2O_2 and the excess of H_2O_2 is destroyed by boiling. The soln. is treated in a separating-funnel with ammonium acetate and extracted with CCl_4 (3×20 ml). If the sample contains more

than 0.05% of Fe, cupferron and 5 ml of acetylacetone are added before the CCl_4 extraction. The combined extracts are washed with 100 ml of acidified water and, after the addition of 100 ml of water, are neutralised to phenolphthalein with NaOH. Borate buffer (20 ml) is added to adjust the pH to 8, 20 ml of tetramethylethylenedithiocarbamate soln. and 5 ml of a 10% soln. of Na K tartrate in methyl propyl ketone are then added and the soln. is shaken vigorously for 5 min. The aq. phase (which contains the Sn^{IV}) is removed and the CCl_4 soln. is treated as before. The aq. extract is adjusted to pH 4 with acetate buffer, and the yellow soln. is extracted with CCl_4 (3×12 ml). The combined extracts are filtered into a 50-ml measuring flask and diluted to vol. with CCl_4 . The colour is then measured photometrically. For lead and lead alloys the sample is treated with 40 to 200 ml of H_2SO_4 (sp. gr. 1.84), according to the size of the sample, fumed to a watery consistency, cooled and diluted carefully. With more than 0.01% of Sn, PbSO_4 is filtered off. The filtrate is further oxidised with a few ml of H_2O_2 . The excess of H_2O_2 is boiled off and the soln. is reduced to about 150 ml. The soln. is treated with 30% ammonium acetate soln. (30 ml), and the procedure for Zn is used.

CHEM. ABSTR.

72. Rapid gravimetric method for the determination of lead as lead phosphate. M. Vancea and M. Volușniuc (Inst. of Chem., Cluj, Romania). *Stud. Cercet. Chim., Cluj*, 1958, 9 (1-4), 155-158.—*Procedure*—To 50 ml of a soln. containing 0.1 to 0.2 g of $\text{Pb}(\text{NO}_3)_2$ is added 5 ml of buffer soln. (6 ml of glacial acetic acid and 13.6 g of Na acetate per litre). To the boiling soln. is added, with continuous stirring, 50 ml of a boiling 3% soln. of $(\text{NH}_4)_2\text{HPO}_4$, and the boiling is continued for 2 to 3 min. The ppt. is filtered off immediately and washed 6 to 7 times with boiling H_2O . After oven-drying, the ppt. is calcined for 5 min. at 800° and then weighed as $\text{Pb}_3(\text{PO}_4)_2$. Alternatively, the ppt. is washed with boiling H_2O , then with ethanol and diethyl ether or acetone, dried *in vacuo* or between 110° and 180° ($>200^\circ$), and finally weighed as the monohydrate. This reduces the time for a determination from 90 to 30 min. The insolubility of the phosphate in acetic acid medium enables Pb^{2+} to be separated from Mg, Zn, Mn, Co, Cd, Cu, Ag and the alkaline-earth metals, with errors $\pm 0.07\%$.

H. SHER

73. Polarographic determination of lead in ascorbic acid medium. W. Czarnecka and A. Sobkowska (Dept. of Anal. Chem., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1958, 3 (3-4), 501-504.—Traces of Pb (10^{-8} to 10^{-6} g per ml) are determined polarographically in the presence of ascorbic acid. A well-defined wave is obtained at ≈ -0.45 V at a pH of ≈ 4 . Nitrates, acetates, tartrates and chromates do not interfere. The interference of UO_2^{2+} and Ti^{3+} is overcome by precipitating Pb as the sulphate. The mean error is $\pm 4\%$ for concn. of 10^{-8} to 10^{-4} g per ml.

H. DMOWSKA

74. Ultra-violet spectrophotometric determination of tin(IV) as a chloro complex. Masayoshi Ishibashi, Yuroku Yamamoto and Yasushi Inoue. *Bull. Inst. Chem. Res. Kyoto Univ.*, 1959, 7 (1), 38-47.—The u.v. absorption spectrum of Sn^{IV} in HCl soln. was studied, the effects of temp., time of standing and interfering ions being investigated. A method which is claimed to be accurate over the range of 0.1 to 10 p.p.m. of Sn^{IV} is described and depends

on the measurement of the absorption at 215 m μ in a soln. 1-5 N with respect to H^+ and 6 M with respect to Cl^- , prepared from HCl and MgCl_2 . Arsenic, Sb, Fe, V and Ti interfere. The absorbance increases with increasing temp., which should therefore be kept constant.

G. S. ROBERTS

75. Photometric determination of titanium as the molybdophosphotitanium complex. R. M. Veltsman (All-Union Sci. Res. Inst. of Hard Alloys). *Zavod. Lab.*, 1959, 25 (4), 408-411.—To determine Ti in the absence of V and Nb the soln. (20 ml) of the sample in dil. H_2SO_4 (1:4) containing from 1 to 20 mg of Ti is mixed with 10 ml of 5% $(\text{NH}_4)_2\text{HPO}_4$ soln., 20 ml of 5% K citrate soln. and 2 g of boric acid, and treated with 25% aq. NH_3 in the presence of Congo red paper so that there is an excess of >5 ml added. An aliquot (20 ml) of the diluted soln. (200 ml) is neutralised with dil. H_2SO_4 (1:4) so that the paper just turns blue, and then treated with 3 ml of 10% $(\text{NH}_4)_2\text{MoO}_4$ soln. and diluted to 100 ml. An aliquot (20 ml) of the yellow soln. is treated with ≈ 0.1 g of KH_2PO_4 and 25 ml of dil. H_2SO_4 (1:4), followed by 1 ml of 0.2% SnCl_2 soln. and dilution to 100 ml. The extinction is measured with a red filter. With complex carbides a 0.1-g sample is heated with 20 ml of dil. H_2SO_4 (1:4), 10 ml of 5% $(\text{NH}_4)_2\text{HPO}_4$ soln. and 20 ml of 30% H_2O_2 , and finally evaporated to fuming. The cooled liquid is treated with 20 ml of 5% K citrate soln., then mixed with an equal vol. of water and 2 g of boric acid. Neutralisation with aq. NH_3 , etc., follows. The method is sensitive to 7×10^{-4} g of Ti in 200 ml.

G. S. SMITH

76. Determination of aluminium in titanium and its alloys by ion-exchange chromatography. B. S. Tsylvina and O. V. Kon'kova (State Sci. Res. Inst. of Rare Metals). *Zavod. Lab.*, 1959, 25 (4), 403-405.—The soln. (0.75 N in HCl) is passed through a column of KU-2, and Ti is washed through with 0.75 N HCl. The Al retained on the column is liberated by elution with 3 N HCl. The method is suitable for contents of Al of 4 to 5% in alloys of Ti and of 0.002 to 0.4% in titanium metal.

G. S. SMITH

77. Direct determination of oxygen and nitrogen in titanium and its alloys. Use of bromine trifluoride. W. A. Dupraw and H. J. O'Neill (Armour Res. Foundation, Illinois Inst. Tech., Tech. Center, Chicago, U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1104-1107.—Low concn. of residual O (0.05 to 1%) and N (0.006 to 0.2%) in metals and alloys can be determined by treatment of the sample with purified BF_3 , removal of the halide products by freezing, and volumetric measurement of the released gases, N being obtained by difference after the removal of O by reaction with copper at 400° . The nickel and glass apparatus used is a slight modification of that of Hoekstra and Katz (*Anal. Chem.*, 1953, 25, 1608); three consecutive samples can be analysed without dismantling. The values for O agree well with those obtained by the vacuum-fusion method; the mean relative deviation is 4.8% (49 analyses). Provided that Fe and Al are absent, the values for N agree satisfactorily with those by the Kjeldahl method. The procedure should also be applicable to the determination of other gases in metals.

W. J. BAKER

78. Spectrographic determination of hafnium in ores and minerals. E. S. Kostyukova. *Sb. Nauch. Trud. Irkutsk. Nauch. Inst.*, 1958, (7), 20-24; Ref.

Zhur., Khim., 1959, (9), Abstr. No. 31,006.—To improve the evaporation of substances from a carbon crater, additional heating of the electrode by a.c. is used. A hole is drilled in the side of the carbon rod (diam. 12 to 14 mm) perpendicular to its axis; the electrode and the test material are introduced through this opening. A current is passed through the horizontal carbon electrode to raise its temp. to 1100° to 1200°, then an arc of 10 amp. is produced between the electrode holding the test substance (anode) and the upper carbon rod, the current being increased to 25 amp. during 10 to 15 sec. After 2 to 2.5 min. the evaporation is accomplished with a far more uniform entry of the test substance into the discharge than by evaporation without heating. This leads to the reduction of the error which can be as high as 7 to 8%. In an analysis, the ratio of sample to buffer mixture (1 part of CaO and 1 part of carbon powder with 4% of U as U_3O_8) is 1:1. Spectra are photographed on type-2 plates, with a large or medium spectrograph; standards are prepared in a basal medium of SiO_2 . Calibration curves are constructed for the lines Hf 2866-37 Å vs. U 2870-97 Å and Zr 2905-22 Å vs. U 2870-97 Å for the concn. range 0.01 to 3%.

K. R. C.

79. Determination of thorium in ores by liquid-liquid extraction. D. A. Everest and J. V. Martin (National Chem. Lab., Teddington, Middx., England). *Analyst*, 1959, **84**, 312-317.—The sample is fused with KOH and the melt is dissolved in dil. HNO_3 according to a specified procedure. Aq. NH_3 is added and the collected ppt. is dissolved in dil. HNO_3 . The vol. of the cooled soln. is adjusted so that 10 ml = 0.8 to 1.6 mg of ThO_2 . Into each of a number of extraction tubes are placed 19 g of $Al(NO_3)_3 \cdot 9H_2O$ and 0.2 g of mesotartaric acid. To one tube, water (8.5 ml) and conc. HNO_3 (1.5 ml) are added, to the next two, water (5.5 ml), HNO_3 (1.5 ml) and the standard soln. [a soln. of $Th(NO_3)_4 \cdot H_2O$ = 1.2 mg of ThO_2 per ml], and to the remaining tubes 10-ml aliquots of the sample soln. The tubes are warmed to dissolve the solid reagents, then cooled, and the contents are extracted with 20 ml of a mixture of tri-*n*-butyl phosphate and ethyl methyl ketone (1:9). Aliquots (10 ml) of the organic extracts are extracted with water, and the combined aq. extracts are treated with conc. HCl (2 ml), an aq. soln. of thoron (0.2%, 5 ml) and ethanol (20 ml). Each vol. is adjusted to 100 ml, and after 4 min. the extinctions are measured at 550 m μ . The simultaneous inclusion of standards is preferable to the use of calibration graphs. A modification for application to thorites is described.

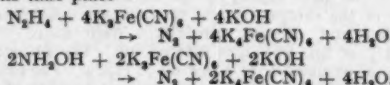
A. O. JONES

80. Quantitative determination of adsorbed sulphates on thorium by means of infra-red spectroscopy. L. G. Tensmeyer and M. E. Wadsworth (Inst. for the Study of Rate Processes, Univ., Salt Lake City, Utah). *U.S. Atomic Energy Comm., Rep. AECU-4076*, 1959, 17 pp.—By using the potassium bromide disc technique, it is possible to apply i.r. analysis quantitatively to the determination of species adsorbed from aq. soln. on solids of large specific area. Adsorption of sulphates on to thorium from aq. sulphate soln. gave a characteristic i.r. spectrum with absorbance bands occurring at 8.4, 8.9 and 9.6 μ . Absorbance measurements at these wavelengths were accurate to within 2% and were directly proportional to the amount of adsorbed sulphate in the disc, after compensation for thorium and sulphate crystallised in the drying process.

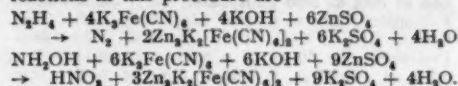
The method was used on samples of thorium having areas > 10 sq. metres per g, and as little as 0.5 μ mole of sulphate can be determined.

NUCL. SCI. ABSTR.

81. Oxidation of hydroxylamine by ferriyanide in presence of zinc sulphate. Rapid method for estimating hydroxylamine and hydrazine in a mixture. Bharat R. Sant (Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chim. Acta*, 1959, **20** (4), 371-375.—A soln. containing hydrazine (1.4 to 6.4 mg) and hydroxylamine (1.9 to 7.6 mg) is titrated by two methods. (i) An excess of standard $K_2Fe(CN)_6$ soln. is added, followed by 25 to 30 ml of borax-boric acid buffer (pH 8 to 9); after 15 to 30 min. the excess of $K_2Fe(CN)_6$ is titrated iodimetrically, or the $K_2Fe(CN)_6$ formed is titrated with standard $Ce(SO_4)_2$ soln. The following reactions take place—



(ii) A known vol. of standard $K_2Fe(CN)_6$ soln. is titrated hot with the soln. of hydrazine and hydroxylamine sulphates in the presence of $ZnSO_4$ and at an alkalinity equiv. to 0.5 to 0.8 N KOH. The end-point is shown by a pure white ppt. The reactions in this procedure are—



The hydrazine and hydroxylamine can then be calculated from the respective vol. of $K_2Fe(CN)_6$ soln. consumed in the two titrations. H. N. S.

82. Mass spectrum of nitric acid. R. A. Friedel, J. L. Shultz and A. G. Sharkey, jun. (Bureau of Mines, U.S. Dept. of the Interior, Pittsburgh, Pa.). *Anal. Chem.*, 1959, **31** (6), 1128.—Reproducible spectra were obtained only after conditioning the instrument with NO_2 or HNO_3 . Spectral analyses of two-component mixtures of red-fuming HNO_3 and NO_2 have been performed successfully. The method is suitable for the analysis of the vapour phase, or of trace quantities of liquid.

K. A. PROCTOR

83. Determination of nitrites and oxides of nitrogen. L. A. Mokhov, Yu. F. Udalov and V. S. Khalturin. *Lab. Delo*, 1959, **5** (2), 45-46.—*Procedure for nitrites*—Add 0.0005% *p*-aminobenzoic acid soln. (1 ml) and 2 N HCl (0.1 ml) to the test soln. (e.g., water drawn from meat) (5 ml) and set aside for 5 to 10 min. Add a 0.1% soln. (0.5 ml) of 8-amino-1-naphthol-3:6-disulphonic acid (I) in 1% Na_2CO_3 soln., set aside for 15 to 20 min. and measure colorimetrically against a standard $NaNO_2$ soln. *Procedure for oxides*—Pass the sample, for example of an industrial atmosphere, through a soln. of *p*-aminobenzoic acid and 2 N HCl, and determine colorimetrically after treatment with I, as described above.

K. R. C.

84. Determination of small amounts of nitrite in food and tissues with a procaine-thymol coupling reaction. H. Lichtenberg (National Criminal Board, Hanover, Germany). *Arch. Kriminol.*, 1958, **121**, 63-65 (in German).—Make 1.5 to 2.0 g of the sample into a pulp, filter, centrifuge, and dilute to 50 ml. Deproteinise the filtrate with

3 to 5 ml of 20% trichloroacetic acid soln. and re-filter (if cloudy, extract with diethyl ether). Add 2 ml of N HCl and filter, then add 0.5% aq. procaine hydrochloride soln. with vigorous shaking, and cool. After 3 min., add 1 ml of 1.5% ethanolic thymol soln. and 1 ml of 40% NaOH soln., with occasional shaking. Measure the extinction of the red azo dye at 450 $m\mu$ against a blank containing deproteinised sample and water. Determine the nitrite concn. by reference to a standard curve (1 to 20 μg of nitrite per ml). The colour is stable. The reagents do not absorb at 450 $m\mu$.

CHEM. ABSTR.

85. Colorimetric determination of phosphorus in the ash of solid fuels. Z. Flum (Anal. Lab., Inst. for Res. of Solid and Gaseous Fuels, Prague). *Paliiva*, 1959, 39 (4), 126-129.—The use of the Belcher method (*Fuel*, 1950, 29, 232) for fuels with high phosphorus contents (0.3%) was studied, and the influence of acidity, nitrates, Fe and As was examined. *Procedure*—Moisten 0.05 g of the finely powdered ash (0.1 g for <0.1% of P_2O_5) in a platinum crucible with conc. HNO_3 (2 ml) and HF (1 ml). Evaporate to dryness and repeat the procedure. Remove the excess of HF by evaporating with HNO_3 (1 ml) and dissolve the residue in H_2SO_4 (20%) (5 ml) by slightly warming (5 min.). Filter, wash the residue with hot H_2O , reduce Fe^{3+} in the filtrate with $Na_2S_2O_4$ soln. (4%) (2 ml), remove SO_2 by boiling, cool and dilute to 100 ml. Convert the phosphate into molybdophosphoric acid, reduce it with $SnCl_2$, and determine the molybdenum blue photometrically by Belcher's method. The ash of 17 varieties of coal was analysed with good results. Nitrates, Fe^{3+} (after reduction) and As do not interfere. J. ZYKA

86. Analysis of phosphate mixtures by paper chromatography. Recent improvements in technique. M. J. Smith (Dept. of Chem., Ontario Res. Foundation, Toronto, Canada). *Anal. Chem.*, 1959, 31 (6), 1023-1025.—Increased precision and accuracy in the analysis of phosphate mixtures and glasses are attained by replacing the descending-flow apparatus by an ascending solvent-system [isopropyl alcohol - 25% trichloroacetic acid - water - 25% aq. NH_3 (7:2:1:0.03) or isopropyl alcohol - isobutyl alcohol - water - 25% aq. NH_3 (40:20:39:1)] operating at 4°. The bands are eluted with 0.1 N aq. NH_3 , and P is determined spectrophotometrically at 830 $m\mu$ (slit width 0.04 mm) by the method of Lucena-Conde and Prat (*cf. Anal. Abstr.*, 1957, 4, 3911), which requires only one reagent. Because the basic solvent carries ring structures farthest, a two-dimensional base - acid run is used to separate mixtures containing cyclic and linear structures. The coeff. of variation is $\approx 1\%$ (18 analyses). W. J. BAKER

87. Quantitative evaluation of paper chromatograms of condensed phosphate mixtures using modified solvents and a densitometer. D. N. Bernhart and W. B. Chess (Victor Chemical Works, Chicago Heights, Ill., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1026-1028.—Ebel's acid solvents (*cf. Anal. Abstr.*, 1954, 1, 283) are modified to ensure a clearer and more rapid separation of the phosphate mixtures. For commercial Na_3PO_4 , detergents and samples containing not more than five components, the solvent system 20% trichloroacetic acid - H_2O - acetone (5:2:13, by vol.) is used, the chromatogram being run for 2 hr. at 25° or 3 hr. at 10°. For

mixtures containing from 5 to 10 components, the same solvent (25:17:58, by vol.) is used for 16 hr. at 10°. The dry chromatogram is sprayed on both sides with acid molybdate soln. and again (after drying) with dil. $SnCl_2$ soln. The 1-in. strips containing the blue molybdophosphate bands are then cut out and passed through a densitometer (Spinco Analytrol, with matched pair of red filters) to obtain curves with sharp maximum peaks. The percentage of each component is calculated from the curves.

W. J. BAKER

88. Quantitative determination of traces of pyrophosphate in orthophosphates. [I.] C. D. Schmulbach (Pennsylvania State Univ., University Park, U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1116.—The rapid colorimetric method of Chess and Bernhart (*Anal. Chem.*, 1958, 30, 111) for determining <1% of $P_2O_7^{4-}$ in the presence of PO_4^{3-} is said to be invalid below $\approx 0.1\%$ (w/w) of $P_2O_7^{4-}$ as $Na_2H_2P_2O_7$; moreover, there is serious interference by Al, Fe and some bivalent metals found in commercial samples. A more reliable separation can be made chromatographically by placing 150 μl of soln. (≈ 2.5 mg of solid sample) in 30 spots along a line 16 cm long and locating the weak $P_2O_7^{4-}$ bands by the aid of reference spots on both sides. The quant. evaluation is made as described by Karl-Kroupa (*Anal. Chem.*, 1956, 28, 1091), together with a calibration curve for the pyrophosphate.

[II.] W. B. Chess and D. N. Bernhart (Victor Chem. Works, Chicago Heights, Ill.). *Ibid.*, 1959, 31 (6), 1116.—In a reply to the criticisms given above, an anion-exchange chromatographic procedure is described for 25-mg samples. All the PO_4^{3-} are eluted from the column (Dowex 1-X8, 100 to 200 mesh) with 300 ml of soln. (0.05 M in HCl and 0.1 M in KCl) at a rate of 15 to 18 ml per min. The polyphosphates are then eluted with 100 ml of M KCl at the same rate and, after acid hydrolysis, are determined colorimetrically. The accuracy and sensitivity are increased by the larger size of sample. W. J. BAKER

89. Rapid precipitation method for the determination of phosphate and sulphate in the presence of each other. E. Bakács-Polgár and L. Szekeres (Inst. f. Chem. d. Tierärztl. Hochschule, Budapest). *Z. anal. Chem.*, 1959, 166 (6), 406-410.—The soln. containing 10 to 100 mg of PO_4^{3-} and 10 to 100 mg of SO_4^{2-} (as alkali-metal salts) in 10 ml is treated with 2 ml of buffer soln. (50 g of NH_4Cl and 400 ml of conc. aq. NH_3 per litre) and 2 ml of ethanolic Indicator (1% of Eriochrome black T in solid KCl) (15 to 20 mg) is added and the PO_4^{3-} are titrated with 0.1 M $MgCl_2$ to a red - violet end-point. The colour is discharged by adding 0.1 M EDTA (one drop in excess) and the SO_4^{2-} are determined by titration with 0.1 M $BaCl_2$. T. R. ANDREW

90. Determination of arsenic in technical sulphuric acid. G. Geitner (Lab. der Luitpoldhütte A.-G., Amberg, Germany). *Brennstoffchem.*, 1959, 40 (3), 89.—The sample (100 g) is diluted, aq. $FeCl_3$ - HCl [121 g of $FeCl_3 \cdot 6H_2O$ and 20 ml of HCl ($d = 1.19$) per litre] and bromine water are added and, when the oxidation is complete, $FeAsO_4$ is pptd. by adding a slight excess of aq. NH_3 . After settling, filtration and washing with hot water, the ppt. is dissolved with hot aq. HCl (1:8). The soln. is then further acidified with HCl (100 ml of conc., and 100 ml of acid of $d = 1.12$), hydrazine sulphate (6 g) and KBr (2 g) are added, and the $AsCl_3$ is

distilled off. The distillate is titrated potentiometrically with aq. 0.07432% KBrO₃ soln. Concentrations from 0.0004 to 0.0091% of As in sulphuric acid were determined with errors $\pm 0.0001\%$.

A. R. PEARSON

91. Application of potassium manganate to quantitative analysis. II. The determination of arsenic(III) and tellurium(IV). G. den Boef, J. den Boef-Nugteren and B. van Laar (Lab. f. Anal. Chem. d. Univ., Amsterdam, Holland). *Z. anal. Chem.*, 1959, **166** (6), 422-426.—Potassium manganate in alkaline soln. (0.5 to 4 N, KOH or NaOH), stabilised by the addition of H₂TeO₄ (3 g per litre), has been used for the potentiometric titration of As^{III} and Te^{IV}. Platinum was used as the indicator electrode and a S.C.E. as reference electrode.

T. R. ANDREW

92. Colorimetric determination of antimony in metallic molybdenum and molybdates. A. I. Lazarev and V. I. Lazareva (Kuibishev Industrial Inst.). *Zavod. Lab.*, 1959, **25** (4), 405-406.—With metallic molybdenum the sample (1 g) is dissolved in a mixture of 10 ml of dil. HNO₃ (1:2) and 4 ml of dil. H₂SO₄ (1:1); the soln. is evaporated to fuming, then diluted, and again evaporated to fuming, followed by cooling and the addition of 10 ml of dil. HCl (1:1), 5 ml of conc. HCl, and 4 g of citric acid (to form a non-reactive complex with the Mo). The soln. is boiled and then kept hot until the pptd. molybdic acid has dissolved. The cooled soln. in a separating-funnel is treated with 4 ml of dil. HCl (1:1) and 3 drops of 10% SnCl₂ soln., then shaken and treated, after 1 min., with 1 ml of 10% NaNO₂ soln., and again shaken during 5 min.; it is then treated with 0.5 ml of satd. urea soln., and shaken for 20 sec.; the gases are allowed to come off, and the mixture is then treated with 60 ml of water and, without shaking, with 0.5 ml of a 0.1% aq. soln. of methyl violet. The funnel is inverted once only, 10 ml of toluene is added, the contents are shaken for 1 min., and after 5 min. the toluene layer is passed through a dry filter into a colorimeter cell. The extinction is measured with a green filter. With molybdates the initial dissolution is suitably modified.

G. S. SMITH

93. Determination of bismuth. P. Spacu and S. Calugareanu (Univ., Bucharest, Romania). *An. Univ. "C. I. Parhon" București, Ser. Științ. Nat.*, 1957, (13), 75-78.—To an aq. soln. of Bi³⁺ in the presence of an excess of KCl add dil. NaOH soln. dropwise until a white ppt. of Bi(OH)₃ appears, then add HCl dropwise until the ppt. is just dissolved. The Bi is now pptd. with an excess of K ethylxanthate, which is added with continuous stirring. The yellow crystals are filtered off, washed with H₂O, then with 50% ethanol, and dried at 60° to 70°. Arsenic, Sb, Cu, Mn, Co, Fe, Ni, Cr, Re, Te, Ag, Hg and Cd interfere, but Na, K, NH₄⁺, Ca, Sr, Ba and Al do not. The error is $\pm 0.3\%$.

CHEM. ABSTR.

94. Rutin as a reagent in inorganic analysis. II. Detection of vanadium(V) with rutin. F. Szarvas and Z. Jarabik (Kossuth Univ., Debrecen, Hungary). *Anal. Chim. Acta*, 1959, **20** (4), 330-331 (in German).—Rutin yields an orange-red colour with V⁵⁺ and the sensitivity of the reaction is increased by the presence of (NH₄)₂S₂O₈ so that 0.3 μ g of V⁵⁺ can be detected in 1 ml of soln. Procedure—To the test soln. (1 ml) add 10%

(NH₄)₂S₂O₈ soln. (1 ml), a 5% soln. of rutin in methanol (1 ml) and 82% H₃PO₄ (3 ml). Of many ions tested only the following interfere in low concn. and they can be masked or reduced with the reagents indicated—Fe³⁺ and Fe²⁺ (EDTA), Ti⁴⁺ (NaF), Ce⁴⁺ and MnO₄⁻ (H₂O₂); the colour of Cr³⁺ also interferes.

H. N. S.

95. Application of the photometric determination of vanadium with catechol in micro-analysis. C. G. Nestler and M. Nobis (Forschungslab. f. Metallkundi. Elektronenmikroskopie, Karl-Marx-Stadt). *Z. anal. Chem.*, 1959, **167** (2), 81-90.—Vanadium, when reduced to V^{IV}, gives a blue coloration with catechol in weakly acid soln. The factors influencing the reaction are discussed, and a method suitable for the determination of V in steel and carbides is described. The sample is dissolved in dil. H₂SO₄ and HCl, followed by conc. HNO₃, and is evaporated to fumes of H₂SO₄. After cooling, the soln. is neutralised with Na₂CO₃ until hydroxides are pptd., and Na₂O₂ is added. The soln. is boiled and filtered. The filtrate contains Cr, Mo, W and V, while the ppt. contains Fe, Mn, Ni, Co and Ti. The filtrate is concentrated and made up to a known vol. An aliquot is neutralised to *p*-nitrophenol indicator with dil. H₂SO₄, and successive additions are made of ammonium acetate soln. (50% aq.) (5 ml), ammonium sulphite soln. (cold satd. aq.) (5 ml) and catechol soln. (20% aq.) (5 ml), and the mixture is made up to 50 ml; after 20 to 40 min. the extinction at 585 m μ is measured against a reference soln. which contains all the reagents except catechol. To eliminate interference by the elements named, as well as the increasing turbidity of the catechol soln., a control soln., containing the same amounts of V, Cr, W and Mo as the sample soln., is analysed at the same time. By this method 5 μ g to 400 μ g of V can be determined, with an accuracy of $\pm 2\%$. The method is claimed to be 8 times as sensitive as the peroxide method.

H. M.

96. Determination of tantalum in niobium. Yu. A. Chernikov, R. S. Tramm and K. S. Pevzner (State Sci. Res. Inst. of Rare Metals). *Zavod. Lab.*, 1959, **25** (4), 398-400.—The sample (1 g) of Nb₂O₅ containing ≈ 0.005 to 0.05% of Ta₂O₅ is fused with K₂S₂O₇, the melt is dissolved in an acid mixture, 0.4 M in HF and 2 M in H₂SO₄, and the Ta is extracted with cyclohexanone (3 \times 13 ml), which is then washed with water (3 \times 3 ml). The Ta is re-extracted into a soln. of ammonium oxalate containing boric acid, and the soln. is evaporated to fuming in the presence of H₂O₂ and H₂SO₄ to oxidise traces of cyclohexanone. The photometric determination of Ta by means of pyrogallol in a mixture of oxalic acid and H₂SO₄ is carried out at 413 m μ . In this medium 500 μ g of Nb gives the same colour intensity as 1 μ g of Ta.

G. S. SMITH

97. Oxygen determination in zinc and magnesium. H. Hartmann, W. Hofmann and G. Ströhl (Tech. Hochsch., Braunschweig, Germany). *Z. Metallk.*, 1958, **49**, 461-463.—The reaction—ZnO + H₂S = ZnS + H₂O was used to determine ZnO in zinc metal by measuring the amount of H₂O formed. Several improvements are now reported, e.g., replacement of H as carrier gas by gettered N. The newly developed apparatus is illustrated. Test runs were performed with high-purity ZnO and evaluated by simultaneous determinations of the ZnS and H₂O formed. The results are tabulated and show the high accuracy of the method. Re-melted zinc and

hard zinc gave O contents of 0.00012 and 0.00028%, respectively. The method was successfully extended to determinations of O in magnesium metal.

CHEM. ABSTR.

98. Studies in qualitative inorganic analysis. XI. Oxidation of hydrogen sulphide to sulphate by nitrate ions. R. Andrews, L. S. Bark and W. M. Dowson (Tech. Coll., Coventry, England). *Mikrochim. Acta*, 1959, (4), 552-557 (in English).—During the pptn. of the sulphide group, the oxidation of H_2S to SO_4^{2-} in the presence of NO_3^- occurs only at high acidities, and then is appreciable only at high concn. of NO_3^- . Thus As^V can be pptd. as As_2S_5 in 6 N HCl provided that the NO_3^- concn. is $\geq M$, a value not likely to be exceeded when working correctly on the semi-micro scale. When As^V is reduced with NH_4I before the passage of H_2S , the oxidation of H_2S in the presence of NO_3^- is negligible. It would seem that loss of the calcium-group metals due to oxidation of H_2S to SO_4^{2-} during qual. analysis is not significant and that any loss observed must arise from other causes.

J. H. WATON

99. Ultra-violet spectrophotometric determination of sulphur dioxide in sulphuric acid. Masayoshi Ishibashi, Yuroku Yamamoto and Yasushi Inoue. *Bull. Inst. Chem. Res. Kyoto Univ.*, 1959, 37 (1), 1-7.—A specific u.v. absorption band observed in conc. H_2SO_4 and with max. at 280 $m\mu$, is due to dissolved SO_2 , and may be used for the analysis of the commercial acid. Over the range of acid concn. from 1 N to 36 N the wavelength of max. absorption moves from 275 $m\mu$ to 280 $m\mu$. At a constant acid concn., Beer's law is obeyed up to ≈ 100 p.p.m. of SO_2 ; As^{3+} , Fe^{3+} and Se do not interfere, but Fe^{2+} seriously affect the accuracy of the method.

G. S. ROBERTS

100. Detection of sulphuric acid in insoluble sulphates. P. Luis (Univ. Nacional, Buenos Aires). *Mikrochim. Acta*, 1959, (4), 541-543 (in English).—*Procedure*—A portion of the sample is mixed with $\approx 10 \mu l$ of 85% H_3PO_4 in a glass tube, one end of which has been drawn out into a capillary. The other end of the tube is sealed, and the tube is heated so as to collect a distillate in the capillary. Care must be exercised to prevent any H_3PO_4 from distilling over. Finally the tube is fused and the capillary drawn off. The distillate is treated on a glass slide with the residue from the evaporation of 3 to 5 μl of 0.25% $CaCl_2$ soln. The slide is then warmed without evaporating the test drop. The presence of SO_4^{2-} is indicated by the appearance of the characteristic needles and plates of $CaSO_4 \cdot 2H_2O$. As little as 0.02 μg of SO_4^{2-} may be identified by this method.

J. H. WATON

101. Modification of a spot test for sulphate ion. Takeo Fukutomi and Michiko Nakahara (Chem. Lab., Univ., Gifu, Japan). *Anal. Chem.*, 1959, 31 (6), 1118.—Feigl's spot test for SO_4^{2-} in the form of alkali salt ("Spot tests. I. Inorganic applications." 4th Ed., Elsevier, N.Y., 1954, pp. 289-290) often gives a pink colour in the absence of SO_4^{2-} because the pH is sufficiently high for phenolphthalein to show its alkaline colour. The use of thymolphthalein in aq. ethanol (1:1) is recommended as being more reliable. The limit of identification is 4 μg of Na_2SO_4 and the dilution limit is 1 in 10^4 .

W. J. BAKER

102. Determination of the sulphate ion with EDTA. II. Chelatometric determination of the sulphate ion as lead sulphate. Nobuhiko Iritani,

Tomoo Tanaka and Hisashi Oishi (Shizuoka Coll. of Pharm., Osaka). *Japan Analyst.*, 1959, 8 (1), 30-33.—Sulphate (5 to 350 μg) is pptd. with a known excess of $Pb(NO_3)_2$ soln. in acetic acid soln. containing 25 to 30% of ethanol, and the filtrate is back-titrated with EDTA in an acetate buffer of pH 3.5 to 4.0, with Cu-1-(2-pyridylazo)-2-naphthol (2% in 50% isopropyl alcohol) as indicator (Flaschka and Abdine, *Anal. Abstr.*, 1957, 4, 361). There is no interference from NH_4^+ , K, Na, Mg, Cl^- or CO_3^{2-} ; Ca and PO_4^{3-} are co-pptd. with $PbSO_4$.

K. SAITO

103. Co-precipitation of sodium in sulphate determination. A spectrographic method. J. L. Voth (Dept. of Chem., Univ. of California, Davis, U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1094-1095.—Spectrographic analyses of $BaSO_4$ pptd. by $BaCl_2$ under different conditions in the presence of a large excess of NaCl show that co-pptn. of Na^+ is not as great as is reported. Minimum co-pptn. ($\approx 0.15\%$ of Na) can be ensured by the sudden addition of $BaCl_2$ soln. (5 or 10%) followed by the hot digestion of the ppt. for ≤ 6 hr. at a pH between 2 and 6; co-pptn. is doubled only at a 20-fold increase in concn. of NaCl.

W. J. BAKER

104. Application of metal-specific indicators to precipitation titrations. IV. The rapid determination of sulphate by titration with standard lead solution. R. Püschel, E. Lassner and P. L. Reiser (Chem. Lab. d. Versuchsanst. d. Metallwerke Plansee A.-G., Reutte, Tirol). *Z. anal. Chem.*, 1959, 166 (6), 401-406.—The pH conditions appropriate to the volumetric determination of SO_4^{2-} with standard soln. of Pb^{2+} have been evaluated for five metal indicators [alizarin red S, diphenylthiocarbazone (II), Xylenol orange, 4-(2-pyridylazo)-resorcinol (II) and Cu^{2+} -EDTA-1-(2-pyridylazo)-2-naphthol]; I and II show the widest pH tolerance and are proposed as indicators for this titration. For an error of $\geq 0.5\%$, the pH ranges are, for I, 3.5 to 5 and, for II, 5.5 to 6.5. The sample soln. should contain 2 to 100 mg of SO_4^{2-} and ≥ 500 mg of $NaNO_3$ or 50 mg of Cl^- . After dilution to 25 ml the soln. is diluted with 25 ml of isopropyl alcohol, and 0.5 g of hexamine is added. The pH is adjusted according to the indicator selected, and the determination is completed by titration with 0.1 N $Pb(NO_3)_2$. Heavy metals, MoO_4^{2-} , WO_4^{2-} , PO_4^{3-} , BO_3^{3-} and F $^-$ interfere.

T. R. ANDREW

105. Analysis of sulphate in chromium plating baths. J. Ducey and G. McKinley. *Plating*, 1959, 46 (4), 384.—A study of the concentration of dissolved sulphate in chromium plating soln. of the 100:1 $CrO_3:SO_3^{2-}$ type as a function of time and temp. showed that all samples should be filtered (or better, centrifuged) before analysis and within 90 min. of removal from the bath.

C. H. COWPER-COLES

106. Determination of a minute quantity of selenium in pyritic ores. Ichi Shiraishi and Minoru Saito (Iwate Univ., Morioka). *Rep. Technol. Iwate Univ.*, 1957, 10, 46-51.—In order to ascertain the behaviour of minute amounts of Se in pyritic ores during metallurgical treatment, some analytical methods already proposed were examined. The colour formed with pyrrole (Hirano et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.*, 1952, 55, 514) was found to be somewhat unstable and confined to the determination of the small amount of Se in the original sample. High accuracy and reproducibility of the results were obtained by distillation of

the Se as the tetrabromide and volumetric determination by iodimetry. The presence of As (0-5%) and Sb (0-2%) caused no interference. The method was applied successfully to the determination of Se in several pyritic ores and the roasted product of chalcopyrite. CHEM. ABSTR.

107. Complexometric titration of molybdenum. I. E. Lassner and R. Scharf (Metallwerke Plansee A.-G., Reutte/Tirol, Austria). *Z. anal. Chem.*, 1959, **167** (2), 114-117.—Molybdenum, reduced to Mo^{IV} with hydrazine sulphate, can be titrated with EDTA soln. As much as 20 times the amount of W can be tolerated if tartaric acid is present. The soln. containing Mo is treated with a known excess of 0.05 M EDTA, then 5 g of tartaric acid and 2 to 3 g of hydrazine sulphate are added. The soln. is acidified with 2 ml of H₂SO₄ (1:1) and boiled for 5 min. Aq. NH₃ is added to pH 4, one-third vol. of ethanol is added, then 5 to 8 drops of 0.1% ethanolic 1-(2-pyridylazo)-2-naphthol soln. as indicator. The soln. is titrated with 0.05 M CuSO₄ to the first violet colour, then 0.05 M EDTA is used to just bring back the yellow colour. H. M.

108. Spectrophotometric determination of molybdenum in uranium alloys. E. F. Jacobson (Watertown Arsenal Lab., Mass.). Rep. WAL-TR-425/1 (Non-AEC), 1959, 12 pp.—The spectrophotometric thiocyanate determination of Mo without extraction was applied to uranium alloys. It was shown to be rapid, accurate and free from interference by alloying elements. A detailed procedure is given. NUCL. SCI. ABSTR.

109. Simultaneous X-ray diffraction determination of molybdenum and tungsten in admixture. W. Glazer (Dept. of Inorg. Chem., Tech. Inst., Warsaw, Poland). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 567-571.—The determination of Mo and W in mixtures by X-ray diffraction is described. The determination is carried out by comparison with standards. H. DMOWSKA

110. Flame-photometric micro-determination of sodium, potassium and calcium in tungsten metal and tungsten oxides. A. Hegedus, J. Neugebauer and M. Dvorsky (Res. Inst. for the Telecommunications Ind., Budapest). *Magyar Kém. Foly.*, 1959, **65** (4), 159-164.—Tungsten metal or WO₃ is removed from the sample by heating it at 600° in a stream of CCl₄ and air, and Na, K and Ca are determined flame-photometrically in the residue. The method is sensitive to 10⁻⁴ to 10⁻⁵ % of Na and 10⁻³ to 10⁻⁴ % of K and Ca in the original sample. The factors influencing the results are discussed; these include the impurities in the sample, the material of the boat from which the W is sublimed and the sublimation temp. A. G. PETO

111. Titration in non-aqueous medium. The use of chromous acetate as a reducing agent. J. Minczewski and S. Kolyga (Dept. of Anal. Chem., Institute of Nuclear Res., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 463-466.—A soln. of chromous acetate in dioxan is used for the potentiometric titration of uranyl salts in an atmosphere of N in non-aq. medium. H. DMOWSKA

112. Radiochemical determination of uranium-237. F. L. Moore and S. A. Reynolds (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1080-1081.—The rapid routine method described, in which no fluoride chemistry is involved,

is applicable to soln. of uranyl sulphate reactor fuel. The U in an aliquot of the sample soln. is pptd. as ammonium diuranate, with ²³⁸U and Zr as carriers; the ppt. is dissolved in HCl and the UO₂²⁺ are complexed in alkaline soln. with hydroxyammonium chloride. After scavenging with Zr(OH)₄ and extraction from HCl soln. into a 5% (w/v) soln. of triisooctylamine in xylene at pH 8, the U is re-extracted into an equal vol. of 0.1 M HCl and re-pptd. as ammonium diuranate. The ppt. is ignited to U₂O₇ and the γ -activity of the ²³⁷U is measured in a well-type scintillation counter. With two cycles of pptn. and extraction, minimum contamination factors from 6 × 10² to 10⁴ can be attained for the chief radioactive nuclides present in the sample. An analysis takes \approx 2 hr.

W. J. BAKER

113. Radiometric determination of uranium content of earth samples. W. L. Schaschkin and J. C. Schumilin. *Chem. Tech., Berlin*, 1959, **11** (1), 16-18.—To determine the uranium content of samples, the β - γ and γ -radiations are simultaneously measured by means of two scintillation counters, Type MC 6, the β -radiation being screened from the γ -ray counter with an aluminium filter (1.5 g per sq. cm). The apparatus is standardised with samples of known uranium or radium content. Equations are given from which the uranium content can be calculated. J. L. PROSSER

114. Application of the 1-(2-pyridylazo)-2-naphthol method of uranium analysis to thorium process solutions. I. H. Spinner and F. C. Miller (Atomic Energy of Canada Ltd., Chalk River, Ontario). Rep. CRDC-837, Atomic Energy of Canada Ltd., 1959, 8 pp.—The described method covers the range 2 to 50 μ g of U and is particularly effective in the presence of a large excess of Th.

NUCL. SCI. ABSTR.

115. Determination of uranium and beryllium in fused fluoride systems. N. E. Rogers and W. D. Prather (Mound Lab., Monsanto Chem. Co., Miamisburg, Ohio, U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1081-1084.—A quant. separation and determination of U (<10 mg) and Be (<4 mg) can be made in the presence of macro amounts of Na in a ternary system of fused fluorides by volatilising the F⁻ as fluoroboric acid during dissolution of the sample with a mixture of conc. HNO₃, H₂BO₃ and conc. H₂SO₄ at 100° and evaporation of the soln. nearly to dryness. The residue is diluted to \approx 275 ml with H₂O and the U^{VI} in the soln. is separated from Be and Na by electrolytic deposition as hydrous oxide for 2 hr. on a platinum-gauze electrode in a soln. of ammonium acetate at 80° to 85° and pH 4. The Be in the plating soln. can then be pptd. as Be(OH)₂ at 65° and pH 8 to 9 (a double pptn. is preferred). Both the deposit of U and the ppt. of Be(OH)₂ are ignited and weighed as oxides. The Na can be determined either by difference or by flame photometry of the filtrate from the Be pptn. Lead, Cu, Sn, Bi, Ag and Cl⁻ should be absent from the soln. during the electro-deposition of the U, and elements that are pptd. by NaOH should be absent when Be is being determined. W. J. BAKER

116. The use of chromous salts for the potentiometric determination of uranium, chromium, iron and vanadium in mixtures. J. Minczewski and S. Kolyga (Dept. of Anal. Chem., Inst. of Nuclear Res., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 467-473.—Chromous sulphate soln. (0.1 N) is used for the potentiometric

titration of V in the presence of Fe^{III} , V^{V} and Cr^{VI} . The inflection points of the curve correspond to the concn. of Cr, Fe and V, and U is determined by difference.

H. DMOWSKA

117. Determination of bromine in uranium fluorides and oxides. R. P. Larsen and N. M. Ingber (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1084-1086.—By the procedure described, 1 p.p.m. of Br can be determined in a 50-g sample; for normal samples (4 to 16 μg of Br) the coefficient of variation is 5%. A preliminary separation from bulk impurities is carried out by distilling the sample with a mixture of 7 M H_2SO_4 and M H_2CrO_4 , solid H_2BO_3 (10 g) being added when F^- are present, and collecting the evolved Br in 1-3% (w/v) Na_2SO_4 soln. A final separation from entrained Cr is made by the re-oxidation of Br^- with cold H_2SO_4 - H_2CrO_4 , followed by the extraction of Br with CCl_4 and its removal from the solvent with an equal vol. of 2 M aq. NH_3 . The aq. layer is evaporated to dryness with 0.1 N NaOH (4 ml), the dry salt is dissolved in H_2O with the addition of 6 drops of 0.1 N H_2SO_4 plus saturated borate buffer (pH 8.7) (2 ml) and 0.1 N $\text{Ca}(\text{OCl})_2$ (100 μl). After shaking for 2 min. and then adding phenol red reagent (10 mg in 1 ml of 0.1 N NaOH, diluted to 100 ml) (200 μl), the bromination is stopped after 4 min. by adding 0.1 N Na_2AsO_4 (500 μl). Acetate buffer (pH 4.6) (1.5 ml) is then added, the vol. is made up to 10 ml with H_2O , and the extinction of the bromophenol red is measured at 590 m μ in a 2-cm cell against a reagent blank.

W. J. BAKER

118. Analysis for plutonium by counting methods. A. M. Aikin and T. Bruce (Atomic Energy of Canada Ltd. Chalk River Project, Ontario). Rep. CEI-58, Atomic Energy of Canada Ltd., 1953, 10 pp.—The LaF_3 method for determining Pu was investigated and found to give results <95% of the true value. The self-absorption of α -particles in Pu sources containing U was measured as a function of the U concn. The absorption reaches 5% when the source contains 500 μg of U. Hence, for soln. of Pu and U, better accuracy is obtained if the soln. is α -counted directly and corrected for self-absorption, than if the Pu is separated by LaF_3 pptn. and counted on the La ppt. The precision decreases as the amount of U in the source increases.

NUCL. SCI. ABSTR.

119. Preliminary report on the X-ray photometric analysis of plutonium in concentrated nitrate solutions. D. M. Newell (General Electric Co. Hanford Atomic Products Operation, Richland, Wash.). U.S. Atomic Energy Comm., Rep. HW-32710 (Del.), 1955. Decl. with deletions, 1958, 5 pp.—The method adopted makes use of an existing technique which has been successful for the determination of U in the presence of many impurities. By using a high concn. of salting agent [5% $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] and an acidity of 1.5 N HNO_3 , the Pu is extracted quant. into tributyl phosphate. A 30% tributyl phosphate in high-purity kerosene (e.g., Deobase) is used. The organic layer is transferred to glass cells with 12 mm path length and read in the X-ray photometer. Interference is caused by U and La; the latter shows no detectable effect except when present in concn. >3% of the Pu concn.

NUCL. SCI. ABSTR.

120. Conditions for the precipitation of trace amounts of plutonium with mandelic acid. E. Merz (Max Planck Inst. f. Chem., Mainz, Germany).

Z. anal. Chem., 1959, **166** (6), 417-422.—Both mandelic acid and β -bromomandelic acid have been studied as pptg. reagents for Pu^{III} and Pu^{IV} in amounts of $\approx 0.01 \mu\text{g}$. By using Yb^{III} as carrier, Pu^{III} is pptd. with about 90% recovery in the pH range 4 to 7 with mandelic acid, or at pH 3 to 7 with β -bromomandelic acid. In soln. of acid concn. of ≈ 0.01 N, Pu^{IV} is recovered with an efficiency of $\approx 90\%$ with Zr^{IV} as carrier. Separations of 0.02 μg of Pu from 500 mg of UO_2Cl_2 are described.

T. R. ANDREW

121. Chemical analysis of ternary alloys of plutonium with cobalt and cerium. G. Phillips and E. Foster (Chem. Div., U.K.A.E.A. (Res. Group), Harwell, Berks., England). A.E.R.E. Report AERE-R2878, 1959, 12 pp.—*Procedure*—The sample (containing ≈ 100 mg of Pu) is dissolved in HCl and an equal vol. of HNO_3 is added. The soln. is allowed to run through a column (7 cm \times 0.6 cm) of De-Acidite FF (-100 to $+200$ mesh), previously washed with 8 N HNO_3 , at a rate of 5 to 6 drops per min. The Pu remains on the column as the anionic nitrate complex. The column percolate, together with the washings with 80 ml of 8 N HNO_3 , is collected and diluted to 100 ml. An aliquot (containing 100 to 300 μg of Co in 1 to 5 ml) is taken, and the Co is determined colorimetrically with nitroso-R salt in 1-cm cells, with either a Spekker absorptiometer (Ilford 604 filter, mercury vapour lamp) or a spectrophotometer (510 m μ). For the determination of Ce, an aliquot containing <25 mg is evaporated to ≈ 5 ml, 10 ml of 0.5% SO_2 soln. and 50 ml of H_2O are added, and the soln. is boiled for 15 min. When cold, the soln. is titrated to a photometric end-point with 0.02 N KMnO_4 in the presence of 100 ml of 11% $\text{K}_2\text{S}_2\text{O}_8$ soln. This is performed at pH 5.5 to 7.0 in a 4-cm cell fitted with a glass superstructure (illustrated). The extinction of the soln. after each addition of KMnO_4 is measured in a Spekker fitted with an Ilford-604 filter. The Pu is eluted from the column with 2 ml of N HNO_3 and 20 ml of 5% hydroxyammonium chloride soln. in N HCl and the eluate is diluted to 25 ml. After setting aside this soln. for 8 hr. in the cold, the Pu is determined photometrically as Pu^{III} in a 1-cm cell at 575 m μ against a blank of 5% hydroxyammonium chloride soln.

J. H. WATON

122. Analytical applications of the ascorbimetric determination of ferricyanide. II. Ascorbimetric determination of free halogens, hypohalites, halites and halates. L. Erdey and G. Svehla (Inst. f. allg. Chem., Tech. Univ., Budapest). *Z. anal. Chem.*, 1959, **167** (3), 164-172.—Free halogens, etc., will oxidise $\text{K}_3\text{Fe}(\text{CN})_6$ (I) to $\text{K}_2\text{Fe}(\text{CN})_6$, which can then be titrated with ascorbic acid. *Procedure for halogens*—Add a soln. containing 2 to 50 mg of Cl, 12 to 200 mg of Br or 150 to 500 mg of iodine to 1 g of I and 2 g of KHCO_3 , shake and set aside for 1 min. Add 1 ml of 0.1% dichlorophenolindophenol soln. (II) and titrate the green soln. with 0.1 N ascorbic acid until colourless. *Hypochlorite*—Mix 15 to 100 mg of ClO^- with 2 g of I and 0.2 g of KI, acidified with 1 to 2 ml of 2 N HCl. When colourless, add 1 g of KHCO_3 and 1 ml of II and titrate. The coeff. of variation is $\pm 0.23\%$ (12 determinations). *Hypobromite*—Mix a weakly alkaline soln. (15 to 100 mg of BrO^-) with 1 g of I and 10 ml of 2 N HCl, neutralise with KHCO_3 and add another 10 ml of acid. Set aside for 1 to 2 min. then add KHCO_3 and II, and titrate. The coeff. of variation is $\pm 0.28\%$ (12 determinations). *Chlorite*—Mix a

0.1 N soln. of ClO_4^- with 2 g of I, a little KI and 10 ml of HCl. Set aside for a few minutes, add KHCO_3 and II, and titrate. Bromate—To 10 to 100 mg of BrO_3^- add 20 ml of HCl and 1 g of I. After 1 to 2 min. add KHCO_3 and II, and titrate. The coeff. of variation is $\pm 0.11\%$ (12 determinations). Iodate—Proceed as for BrO_3^- . The coeff. of variation is $\pm 0.24\%$ (12 determinations). Chloramine T—A weakly acid soln. is used; the reaction is slow unless KI is added. The coeff. of variation is $\pm 0.2\%$ (12 determinations).

P. D. PARR-RICHARD

123. Studies in qualitative inorganic analysis.

X. Separation and identification of the halides and thiocyanate. R. Belcher and W. I. Stephen (Chem. Dept., Univ., Birmingham, England). *Mikrochim. Acta*, 1959, (4), 547-551 (in English).—The addition of $\text{Pb}(\text{NO}_3)_2$ serves to remove I^- and most of the SCN^- ; any excess in soln. is destroyed with NaNO_2 . Bromide is tested for and is removed by heating the soln. with PbO_2 ; then the presence of Cl^- is shown by pptn. with AgNO_3 . In the systematic scheme for the analysis of the anions, the silver salts of these four anions together with $\text{Ag}_3[\text{Fe}(\text{CN})_6]$ and $\text{Ag}_3[\text{Fe}(\text{CN})_5]$ are brought into soln. by metathesis with ammonium sulphide. Procedure—To the ppt. of silver salts are added 10 drops of conc. aq. NH_3 and 3 drops of yellow ammonium sulphide. The ppt. is broken up and the suspension is heated until Ag_2S coagulates. The soln. after centrifuging is boiled and, when it becomes cloudy, 5 to 6 drops of 4 N HClO_4 are added; the soln. is further heated to expel all the H_2S . As a test for I^- , 1 drop of soln. is spotted with iodide-free starch soln. and NaNO_2 soln. on filter-paper; a blue colour indicates I^- . The remainder of the soln. is treated with 5 drops of $\text{M Pb}(\text{NO}_3)_2$. After centrifuging the soln., 1 drop is spotted on filter-paper with 1 drop of 1% $(\text{NH}_4)_2\text{SO}_4\text{Fe}_2(\text{SO}_4)_3$ soln.; a red colour indicates SCN^- . The excess of I^- and/or SCN^- is removed from soln. by boiling with 3 to 4 drops of 20% NaNO_2 soln. until no more NO_2 is evolved. When the soln. is cool, 2 to 3 drops of 4 N HClO_4 are added and a little PbO_2 . On boiling the soln., the expulsion of Br and the red coloration produced with moistened fluorescein paper indicate Br^- . After the complete expulsion of Br, the soln. is set aside for 30 sec. and the supernatant liquid is decanted and tested with AgNO_3 for Cl^- .

J. H. WATON

124. Determination of fluorides by mercurimetric titration of lead chloride fluoride. J. Ullmann. *Publ. Fac. Sci. Univ. Masaryk*, 1958, (390), 33-39.—To a soln. containing 20 to 110 mg of F^- add 10% NaCl soln. (10 ml), dilute to 150 ml with water, neutralise with N HCl and add 3 ml in excess. To this soln., at 55°, add 250 ml of saturated PbCl_2 soln. (I), filter off the ppt. after 30 min., wash it with I (5 ml), then with 30% ethanol (2 ml), and finally with 80% ethanol (3 ml). Dissolve the ppt. by washing it with 50% HNO_3 (100 ml) at 40° and then with hot water. Add some solid sodium nitroprusside and titrate the soln. with standard $\text{Hg}(\text{NO}_3)_2$ soln. until the first turbidity is observed by means of the Tyndall effect.

CHEM. ABSTR.

125. Determination of fluorine in cryolite and aluminium fluoride. J. Bognár and L. Nagy. *Kohászati Lapok*, 1958, 91, 96-98.—An argentimetric method with potentiometric titration was developed to enable determinations to be made that were accurate to within $\pm 0.1\%$ and gave replicate

results within 0.3%. Procedure—Mix a 0.25-g sample thoroughly with 1 g of quartz powder and 4 g of a mixture of Na_2CO_3 and K_2CO_3 and fuse in a platinum crucible at $< 700^\circ$. When no more CO_2 is evolved (15 to 30 min.), cool and suspend the residue in 100 ml of hot water in a 300-ml beaker. Set aside for 2 hr., filter the suspension and dilute the filtrate to 250 ml. Dilute 50 ml of this soln. to 100 ml, add N HCl until the soln. is red to methyl orange, heat to 70°, and add slowly, with stirring, 100 ml of 1% PbCl_2 soln. heated to 70°. To the soln., now containing a ppt., add 0.2 N NaOH until a yellow colour appears, then set aside for 24 hr. Collect the ppt. on a G-3 glass filter, wash three times with saturated PbCl_2 soln. (prepared by diluting 20 to 25 ml of 1% NaF soln., adding 2.5 g of NaCl, neutralising with N HCl, pptg. PbCl_2 with PbCl_2 , and saturating water with the washed ppt.), and twice with 50% ethanol. Dissolve the ppt. in 10 ml of 25% HNO_3 in a 200-ml beaker and titrate potentiometrically with 0.1 N AgNO_3 .

CHEM. ABSTR.

126. Analysis of bromine trifluoride, bromine pentafluoride and uranium hexafluoride utilising high-resolution nuclear magnetic resonance spectra. J. N. Shoolery, E. I. Goodman and J. Littman (Brookhaven National Lab., Upton, N.Y.). *U.S. Atomic Energy Comm., Rep. BNL-2382*, 1957, 4 pp.—It was found feasible to analyse mixtures of BrF_3 , BrF_5 and UF_6 in the concn. ranges studied by nuclear magnetic resonance techniques without the necessity of handling materials outside of their Teflon containers. The method was rapid, sensitive and accurate.

NUCL. SCI. ABSTR.

127. Titrimetric determination of hydrogen present as water and/or hydrogen fluoride in uranium tetrafluoride and magnesium fluoride. W. M. Wise (Mallinckrodt Chem. Works, St. Charles, Mo., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1001-1003.—The sample is ignited in a furnace at 500° and the H_2O and HF, volatilised into a stream of dry N, are passed over solid Na_2CO_3 at 300° so that the HF reacts to form H_2O . The water vapour is then bubbled through a measured vol. of Karl Fischer reagent, the excess of which is titrated with a standard soln. of H_2O in methanol. Concn. of H of ≈ 35 p.p.m. can be determined with a precision at the 95% confidence level of $\pm 13\%$ for UF_4 and $\pm 16\%$ for MgF_2 .

W. J. BAKER

128. Colorimetric determination of traces of chlorides. W. Kemula, A. Hulanicki and A. Janowski (Dept. of Inorg. Chem., Warsaw Univ., Poland). *Chem. Anal., Warsaw*, 1958, 3 (3-4), 581-585.—Chlorides in concn. of 3 to 50 μg are determined colorimetrically with mercury diphenylcarbazone. The interference of Cu and Fe can be eliminated by the addition of triethanolamine. The accuracy of the determination depends on the temp. and on the addition of protective colloids to stabilise the colour. Errors are $\leq \pm 5\%$.

H. DMOWSKA

129. The micro- and macro-determination of perchlorates. Z. Zagórski and W. Krawczyk (Central Lab. of Accumulators and Cells, Poznań, Poland). *Chem. Anal., Warsaw*, 1958, 3 (3-4), 505-512.—Perchlorates are reduced to chlorides by being heated under reflux with H_2SO_4 , $\text{Ti}(\text{SO}_4)_2$ and metallic zinc. The chlorides (micro amounts) are determined turbidimetrically with AgNO_3 or (macro amounts) polarographically after oxidation of the Ti with sodium perborate.

H. DMOWSKA

130. Extraction of ferric chloride with ethyl acetate. Tadashi Fujinuki (Geol. Survey of Japan, Hisamoto-cho, Kawasaki, Kanagawa-ken). *Japan Analyst*, 1959, 8 (1), 34-39.—The extraction of FeCl_3 with ethyl acetate was examined with reference to the decomposition and solubility of this ester in water. In 6 N HCl (optimum concn.) three extractions suffice for the complete removal of Fe. The concn. of HCl thus decreases to 4.5 N, and its extraction into the organic layer is $\approx 10\%$. The presence of < 1 ml of H_2SO_4 , HClO_4 and H_3PO_4 and < 10 ml of 14 N HNO_3 in 10 ml of 6 N HCl does not affect the extraction. Ethyl acetate can be used in place of diethyl ether, especially in the presence of Al, Ca, Mg, Cu, Ni, Zn, Co, Mn, Th, Ti and Zr, and the method is recommended for use in the rapid analysis of iron ore or steel or mineral deposits.

K. SAITO

131. Diphenylthiovioluric acid as a reagent for gravimetric estimation of metals. II. Estimation of iron. R. P. Singh (Chem. Dept., Univ., Delhi). *J. Indian Chem. Soc.*, 1959, 36 (1), 57-58.—Diphenylthiovioluric acid is a suitable reagent for the gravimetric determination of Fe^{3+} and Fe^{2+} . The quant. pptn. of the Fe^{3+} complex is carried out on a water bath at pH 4.9 to 5.6 in the presence of a small amount of quinol (to prevent oxidation), and of the Fe^{2+} complex similarly at pH 4.9 to 5.8, but without quinol.

I. JONES

132. Induced reactions in analytical chemistry. I. General discussion on the induced reaction and on the mechanism of the KMnO_4 - Fe(II) - Cl^- system including the suppression with Zimmermann-Reinhardt reagent. Masayoshi Ishibashi, Tsunenobu Shigematsu and Shozo Shibata (Gov. Ind. Res. Inst., Hirate-machi, Kita-ku, Nagoya). *Japan Analyst*, 1959, 8 (1), 17-20.—In a discussion of the mechanism of induced reactions and their suppressing action in oxidation-reduction titrations, the concept of an "inductive actor" is introduced, additional to those of actor, inductor and acceptor. The most important controlling factor is the formation of this inductive actor from the actor, which is regarded as self-induction, as distinct from the mutual induction caused by the inductor. In the system KMnO_4 - Fe^{II} - Cl^- , the actor is Mn^{VI} , the inductor is Fe^{II} , the acceptor is Cl^- and the inductive actors are Mn^{VI} and Mn^V , which are produced from KMnO_4 by Fe^{II} , and oxidise Cl^- to ClO^- . The Mn^{II} in the Zimmermann-Reinhardt soln. causes the rapid disappearance of Mn^{VI} by reducing it to Mn^{IV} and Mn^{III} .

K. SAITO

133. Analysis for iron in silicates with sulphosalicylic acid. I. A. Voinovitch and J. Debras (Lab. Chim. Soc. Franc. Céram., Paris). *Ind. Céram.*, 1958, (500), 257-261.—The colorimetric method described is compared with the volumetric TiCl_3 method. The colorimetric method is used to determine both Fe^{II} and Fe^{III} ; it is rapid, sensitive and precise, and is not influenced by Si, Ca, Mg, Na, K, Al or Ti in quantities normally found in silicates. The stability of the colour complex is good and the plot of colour density vs. concn. is linear from 0.02 to 25 p.p.m. As in the volumetric method, Mn and Cr interfere slightly. In high concn. TiO_2 slightly increases and Al_2O_3 decreases the results. The silicate sample is dissolved by alkali fusion or by acid reaction. For the alkali treatment, use a 100 to 200-mg sample with a ratio of sample to melt of 1:5 to 1:10. For the acid treatment, use 200 to 1000 mg of sample with H_2SO_4 (2 ml) and 40%

HF (20 ml). Evaporate to dryness, and repeat the acid treatment, then heat to fumes of H_2SO_4 . Cool, dissolve in 50 to 100 ml of water, add 10 to 15 ml of HCl and boil for 10 to 15 min. Cool, and dilute to 250 or 500 ml. Take an aliquot (≈ 0.002 to 2.5 mg of Fe_2O_3) and transfer it to a 100-ml flask. Add N NH_4Cl (5 ml), 20% sulphosalicylic acid soln. (6 ml), and enough aq. NH_3 (1:4) to change the colour of the soln. from rose to bright yellow, then add 1 ml in excess. Dilute to 100 ml after cooling to room temp. Measure the colour intensity spectrophotometrically at 420 m μ .

CHEM. ABSTR.

134. Determination of iron, chromium and nickel by X-ray fluorescence analysis. Aqueous solution method. W. W. Houk and L. Silverman (N. Amer. Aviation, Inc., Canoga Park, Calif.). *Anal. Chem.*, 1959, 31 (6), 1069-1072.—The procedure is applicable to stainless steel, Ni-Cr alloy, and weld samples. The sample (0.5 g) is dissolved in a mixture of acids (HCl, HNO_3 , HF), the soln. is heated to fuming with HClO_4 , cooled and diluted to 100 ml with H_2O . The intensities of fluorescence radiation for the respective K_α lines are then measured in a 10-ml cell with a scintillation counter fitted with a pulse-height analyser and with the background at 68.5° (2 θ). The times required to record 102,400 counts (for Fe, Cr, Ni and background) are measured and the percentage of each element is calculated from standard curves of ratios of counts to background, and of counts per sec., vs. concn. in mg per ml. The error is < 1.5% and the lower limits of determination are from 5 to 10 μg per ml for each element. If a Geiger counter is used, with the background at 0.6 A, the error is < 3%.

W. J. BAKER

135. Analysis for industry [titrimetric determination of iron and uranium]. A. M. G. Macdonald. *Ind. Chem.*, 1959, 35, 243-245.—A detailed review of recent developments is given. (48 references.) S.C.I. ABSTR.

136. Coulometric determination of sulphur in silicon-iron. L. E. Hibbs and D. H. Wilkins (General Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chim. Acta*, 1959, 20 (4), 344-352.—Sulphur in ferrous materials, in concn. down to $\approx 0.0001\%$, is determined by an adaptation of the conventional combustion procedure, the SO_2 evolved being titrated by two different coulometric methods. Procedure (i)—The SO_2 is absorbed in water and the soln. is added to an acid soln. of KBr containing a small amount of KI. The mixture is titrated coulometrically at constant current, and the generation of the first excess of free iodine, which marks the end-point, is indicated by a sudden increase of current through a pair of platinum indicator electrodes. Procedure (ii)—The SO_2 is absorbed in $\text{K}_3\text{Fe(CN)}_6$ soln. and the Fe(CN)_6^{4-} formed are titrated with electrolytically generated Br. The end-point is shown by an increase of the indicator current.

H. N. S.

137. Rapid spectrometric determination of gases in steel. W. Koch, S. Eckhard and F. Stricker (Max Planck Inst. f. Eisenforsch., Düsseldorf). *Arch. Eisenhüttenw.*, 1959, 30 (3), 137-144.—A direct-reading spectrometric method for the determination of CO, N and H is described. The gases are excited in a high-frequency field and the intensities of their emission spectra are recorded during evacuation. With increasing vacuum these

intensities pass through a maximum, which is proportional to the concn. of the gases in the mixture. Apparatus based on this principle is described in detail. It operates in the spectral range of 3650 to 6500 Å and under a pressure of 0.2 to 10^{-4} torr. A single determination requires 20 sec. and the combined determination of CO, N and H 2.5 to 4 min.

H. SAWISTOWSKI

138. Simultaneous determination of carbon and other impurities in steel and pig-iron by a spectrographic method. A. S. Dem'yanchuk. *Avtomat. Svarka*, 1958, (8), 41-45; Ref. Zhur., *Khim.*, 1959, (5), Abstr. No. 15,103.—In the analysis of low-alloy steel, spectra are produced either under conditions described in a previous paper (Kudelya and Dem'yanchuk, *Zavod. Lab.*, 1954, 20, 583) or by a high-frequency spark discharge. Conditions are given for the determination of Al, V, W, Si, Mn, Cu, Mo, Ni, Cr and C in steel and for the determination of Si, Mg, Mn and Cu in pig-iron. K. R. C.

139. Determination of non-metallic inclusions in low-chromium steel by chlorine methods. Tai-Chung Lee, Shu-Hsi Chao and Tsin-Hua Lu (Inst. of Metal Res., Acad. Sinica). *Acta Metallurg. Sinica*, 1959, 4 (2), 162-168.—A detailed description is given of the use of the electrolytic and chlorine methods [cf. Colbeck et al., *Iron Steel Inst. (London)*, *Spec. Rep.*, 1939, No. 25, 109] in isolating and determining SiO_2 , Al_2O_3 , FeO, MnO, Cr_2O_3 , CaO, MgO and TiO_2 in low-chromium steel and in steel containing >0.5% of C. Samples are heated at 1100° for 40 min. before electrolysis. This is a necessary preliminary in order to facilitate the subsequent decomposition of the sample. Satisfactory results are obtained when chlorination is conducted either at normal or low pressure. Chlorinations conducted at 250° and 550° show no appreciable difference in results.

S. H. YUEN

140. Method for quantitative determination of ferromagnetic impurities in austenitic steel by means of electron diffraction. S. Yamaguchi and T. Hori (Inst. of Phys. and Chem. Res., 31 Kamifugi (Hongo), Tokyo, Japan). *Z. anal. Chem.*, 1959, 167 (3), 193-196.—The Lorentz effect can be used for the measurement of ferromagnetic impurities in special steels, by a double exposure of the polished sample and a non-ferromagnetic substance such as gold. The eccentricity is a measure of the ferromagnetic impurity and is characteristic of the lattice structure.

P. D. PARR-RICHARD

141. Methods of determining hydrogen in relation to the chemical composition and structure of steel. Yu. A. Klyachko and T. A. Izmanova (Central Sci. Res. Inst. of Ferrous Metallurgy). *Zavod. Lab.*, 1959, 25 (4), 396-398.—Vacuum heating for the determination of H is applicable to plain carbon steel of carbon content >0.5%, to chromium steel of carbon content >0.05%, and to steel containing Nb, Ni and Al with no restriction on the content of C. Vacuum fusion is necessary in other cases, including steel containing Ti and Mn.

G. S. SMITH

142. Photometric method of determining vanadium in steel. A. I. Cherkosov and T. S. Zhigalkina (Astrakhan Tech. Inst. of the Fishing Ind.). *Zavod. Lab.*, 1959, 25 (4), 406-408.—The reagent is prepared by adding 0.7 g of NaNO_2 to an ice-cold soln. of 1.73 g of sulphuric acid in 20 ml of 4 N NaOH, then gradually adding 4 N HCl to give an

acid reaction to Congo red, and mixing with a soln. of 1.88 g of 3-hydroxy-2-naphthoic acid in 10 ml of 4 N NaOH, followed by the addition of sufficient 4 N HCl to precipitate the dye, which is then filtered off, washed, and dried in air. For use, the dye is dissolved in 60% H_2SO_4 to form a red soln. The addition of VO_2^- reduces the colour intensity in proportion to the amount added. With contents of V between 5 and 25 µg per ml no interference is caused by Cu, Cr, Al, Co, Ni, Ti, NH_4^+ , Mn, W, the alkali metals, Fe (in the presence of H_2PO_4^-) and Mo (if the Mo to V ratio is >1:2). To determine V in steel, the sample (0.1 to 0.5 g) is dissolved in a mixture of 20 ml of dil. H_2SO_4 (1:3) and 5 ml of dil. HNO_3 (1:1), the soln. is evaporated to fuming, the cooled residue is treated with 100 ml of water and 3 to 5 ml of H_2PO_4^- , and V is oxidised by dropwise addition of 2% KMnO_4 soln., giving a pink colour stable for 1 to 2 min. The soln. is then treated with 1 ml of 4% MnSO_4 soln. and titrated until decolorised with 0.1 N oxalic acid. It is filtered if necessary and diluted to 200 or 250 ml, and 1 ml is transferred to a tube containing 5 ml of a soln. obtained by dissolving 7.0 mg of the dyestuff in 120 ml of conc. H_2SO_4 , adding 60 ml of water, cooling, and diluting to 200 ml. The extinction at 533 mµ is measured after 40 min. The content of V is found by reference to a calibration curve.

G. S. SMITH

143. Use of EDTA (disodium salt) for determining chromium in steel. M. E. Vdovenko and N. E. Spivakovskaya (Inst. of Gen. and Inorg. Chem., Acad. Sci., USSR). *Zavod. Lab.*, 1959, 25 (4), 416-417.—The sample (0.1 to 0.2 g) is dissolved in 20 ml of dil. H_2SO_4 (1:4) with the subsequent addition of a few drops of conc. HNO_3 . The soln. is evaporated to fuming, cooled, diluted with 50 ml of water, and filtered, the insol. WO_3 being washed with dil. H_2SO_4 . The combined filtrates are then treated hot with 1 ml of 1% AgNO_3 soln. and 1.5 to 2 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and boiled for 3 min. after the appearance of the colour of MnO_4^- . The addition of 5 ml of 1% NaCl soln. is followed by boiling for 15 to 20 min. to remove Cl and to destroy the excess of $\text{S}_2\text{O}_8^{2-}$, and the cooled and diluted soln. (150 ml) is treated with 20% Na_2CO_3 soln. to give a pH of 1.5 to 2.0 (methyl violet spot test), then with 1.0 to 1.5 g of KI, followed after 5 min. by the addition of 3 g of EDTA (disodium salt) and 0.5 g of Na acetate. The iodine liberated after 2 min. is titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. The method is applicable to steel samples containing V (≈1%), W (≈20%) and Ni (≈10%).

G. S. SMITH

144. Polarographic determination of molybdenum in steel. M. Habrcetl (Železářny Čenkov, Czechoslovakia). *Hutn. Listy*, 1959, 14 (4), 324-325.—In the presence of EDTA (disodium salt) (I) in an ammonium acetate buffer soln. of pH 4.5 only Cu interferes in the polarographic determination of Mo in steel provided that Fe and some other elements are separated with aq. NH_3 from the sample soln. **Procedure**—Dissolve the finely divided sample (1 g for 0.01 to 1% of Mo) in HNO_3 (1:1) (20 ml), evaporate to dryness, add conc. HCl (10 ml) and evaporate again. The separated residue with H_2O (25 ml) and add, with stirring, conc. aq. NH_3 (20 ml). Cool and dilute to 100 ml with H_2O , mix and filter. To 50 ml of the filtrate add glacial acetic acid (5-5 ml), I (3-7 g) and gelatin soln. (0.5%) (2 ml), transfer to a 100-ml flask, dilute to vol. with H_2O , remove O with a stream of N_2 , and register

the polarographic wave from -0.3 V. Evaluate the results by the use of the method of standard additions. A standard amount of Mo must be added before pptn. with aq. NH_3 to eliminate errors caused by adsorption of Mo on the ppt.

J. ŽYKA

145. The polarographic analysis of iron and steel. I. Determination of molybdenum, tungsten, titanium and niobium in phosphoric acid. Masao Kawahara, Heichi Mochizuki and Rokuro Kajiya (Kawaki Plant, Nippon Yakin Kogyo Co., Daishigawara, Kawasaki, Kanagawa-ken). *Japan Analyst*, 1959, 8 (1), 25-30.—Characteristic polarographic waves are given by molybdate ($\approx +0.1$, -0.35 and -0.78 V vs. the S.C.E.), tungstate (≈ -0.4 V) and Ti ($\approx +0.2$ to -0.2 V) in 1 to 12 M H_2PO_4 , whilst Nb gives a wave (-0.56 V) in $\text{H}_2\text{PO}_4 > 10$ M. The $E_{1/2}$ value increases slightly with increase in concn. of H_2PO_4 and the wave height is proportional to the concn. of metal at a given concn. of H_2PO_4 . The simultaneous determination of W and Nb is effected in 6 M H_2PO_4 containing 14.5 M H_2SO_4 , and that of Ti and W in 1.5 M H_2PO_4 containing 0.01 M EDTA.

K. SAITO

146. Volumetric and gravimetric investigations of cobalt powder. F. Skaupy and A. Herrmann (Paulinenstr. 27, Berlin-Lichterfelde). *Z. anorg. Chem.*, 1959, 299, 338-340.—A volumetric method described earlier (*Ibid.*, 1950, 262, 109) led to some difficulties. A comparison has been made between a gravimetric reduction method and a volumetric titration with KMnO_4 . The commercial powder is reduced with a mixture of N and H (3:1). The reduced powder is heated on a water bath for 10 min. with 4 ml of FeCl_3 soln. (1 vol. of conc. soln. to 1 vol. of H_2O), then 4 ml of dil. H_2SO_4 (1:4) is added and the heating continued for 5 min. The soln. is diluted to 200 ml and a 50-ml aliquot is titrated with 0.1 N KMnO_4 . A blank is carried out without the cobalt. The results agreed with those obtained gravimetrically.

N. E.

147. Metallographic differentiation of cobalt metal, oxide and sulphide. R. S. Young. *Metalurgia, Manch.*, 1959, 59, 210.—Etching of the sample either with HgCl_2 soln. (1%) for 30 sec. or with NaHSO_4 soln. (35%) for 2 min. imparts a brown stain to the metallic phase but leaves unchanged the dark-grey oxide and the yellowish-white sulphide.

N. E.

148. Separation of cobalt from manganese by means of nitroso-R salt on an ionite. L. M. Orlova (Moscow Steel Inst.). *Zavod. Lab.*, 1959, 25 (4), 417.—A cationite column (H form) is used to retain both Co and Mn, and the Co is then eluted with a satd. soln. of nitroso-R salt, followed by water. When the washing water becomes colourless (absence of Co and Fe) the Mn is eluted with 4 N H_2SO_4 and determined by the usual arsenite method.

G. S. SMITH

149. Eriochrome black A as reagent for spectrophotometric micro-determination of cobalt in the presence of nickel. A.-A. M. Amin, A. A. El Raheem and F. A. Ozman (Nat. Res. Centre, Cairo, Egypt). *Z. anal. Chem.*, 1959, 167 (1), 8-16 (in English).—Eriochrome black A (C.I. Mordant Black 1) is a suitable reagent for the spectrophotometric determination of microgram amounts of Co, either in pure cobalt soln. or in the presence of Ni and other cations. The decrease in the absorbance of a soln. of Eriochrome black A produced by Co is measured at 620 m μ in a medium buffered to pH 10

and containing EDTA (disodium salt). The effects of time, temperature, pH, the presence of other cations, and concn. of dye on the formation of the red colour of the Co-Eriochrome black A complex are discussed. In the presence of an excess of EDTA, Ni, Zn, Pb and Ca do not interfere, but Cd, Cu, Ba, Sr, Mn and Mg interfere to varying degrees. The construction of a calibration curve is described. The procedure is accurate to within $\approx \pm 0.061$ μg or $\pm 2.8\%$, even in the presence of about 100 times the amount of Ni. Fair accuracy was observed for concn. as low as 0.9 μg of Co. After modification the method may be applied to the determination of Co in soil and biological materials.

S. M. MARSH

150. Simultaneous spectrophotometric determination of traces of cobalt, nickel and copper with dithio-oxamide. W. D. Jacobs and J. H. Yoe (Virginia Univ., Charlottesville, U.S.A.). *Anal. Chim. Acta*, 1959, 20 (4), 332-339.—Spectral extinction curves show the most advantageous wavelengths for the simultaneous determination of Co, Ni and Cu with dithio-oxamide. The optimum pH is 9.0 ± 0.3 . The constitution of the complexes, the effects of temp. and the order of addition of reagents, the sensitivity of the reactions and adherence to Beer's law were also investigated. The following metals interfere at a 1:1 ratio—Pd, Ag, Pt, Au, Hg and Pb; CN^- must be absent, and a high concn. of citrate or tartrate interferes in the determination of Co and Ni. Cobalt interferes in the determination of Ni when the Co to Ni ratio is $> 1:7$. Gum acacia is used to stabilise the colours obtained with the water-insoluble complexes, and the concn. of Co, Ni and Cu are derived from the extinction values at 440, 640 and 385 m μ by means of a series of equations. The method is applied to the analysis of aluminium alloys and ferrosilicon.

H. N. S.

151. Determination of microgram amounts of cobalt in sodium metal. 2-Nitroso-1-naphthol spectrophotometric method. L. Silverman and R. L. Seitz (Atomic International, Canoga Park, Calif., U.S.A.). *Anal. Chim. Acta*, 1959, 20 (4), 340-343.—Sodium used in atomic reactors must contain > 2 p.p.m. of Co to avoid a long "cooling" period when the reactor is shut down. The method described is suitable for the determination of concn. down to 0.1 p.p.m. Procedure—Treat a 10-g sample under N with an excess of water, added in small portions, and neutralise the resulting soln. with HCl. Add 1 ml of 10% ammonium citrate soln. and sufficient borate buffer (19 g of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 10 ml of conc. aq. NH_3 per litre) to adjust the pH to 6.5. Add 5 ml of a 0.01% soln. of 2-nitroso-1-naphthol, prepared with the use of sufficient N NaOH to dissolve the reagent, shake for 3 min. with 20 ml of CCl_4 and separate. Shake the CCl_4 layer for 15 sec. with 10 ml of 4% NaOH soln. containing 1 drop of 10% KCN soln. to remove the excess of reagent and the complexes of Cu and Ni. Wash the CCl_4 soln. with 10 ml of 1% NaCl soln., filter through cotton and determine the extinction in a 5-cm cell at 535 m μ . Prepare a calibration graph for 0 to 10- μg amounts of Co added to 25 g of NaCl in 100 ml of soln. The presence of Cl^- (< 3 g of NaCl) is necessary for the complete extraction of the Co complex, and gram quantities of NH_4^+ have an adverse effect on its formation.

H. N. S.

152. Separation of nickel and cobalt by paper chromatography. G. R. Weidmann (Kanonenweg 33, Coburg, Bavaria). *Canad. J. Chem.*, 1959, 37

(4), 830-831.—Tri-*n*-butyl phosphate (I)-methanol-HCl is very suitable as solvent for the paper chromatography of the chlorides of Ni and Co. Increasing HCl concn. increases the R_F value of the Co. The rate of movement of the Ni depends on the methanol concn., since Ni is immobile in I. It is recommended that I be equilibrated with HCl (9 to 10 *M*) and mixed with methanol in the proportion of 2:1. J. P. STERN

153. Separation and qualitative and semi-quantitative determination of micro amounts of nickel and cobalt by the Weisz ring-oven method. P. J. Antikainen (Inst. of Chem., Univ., Helsinki, Finland). *Mikrochim. Acta*, 1959, (4), 558-562 (in English).—Both elements are determined by means of their complexes with dimethylglyoxime (II), by employing a filter-paper saturated with an ethanolic soln. of I. The action of aq. NH_3 effects a separation by dissolving the cobalt complex. The sensitivity of the identification for Ni is increased by eluting the nickel complex with an ethanolic soln. of I which contains bromine water; a soluble complex of Ni forms which is extracted to the periphery. The sensitivity of the method is 0.1 μg for Ni and 0.5 μg for Co; the max. amounts that may be used are 100 μg and 20 μg , respectively. J. H. WATON

154. Quantitative determination of nickel in oils by X-ray spectrography. C. W. Diggins, jun., and H. N. Dunning (Petroleum Expt. Station, U.S. Dept. of the Interior, Bartlesville, Okla.). *Anal. Chem.*, 1959, 31 (6), 1040-1042.—The use of cobalt as an internal standard in this rapid and direct procedure minimises the effects of the matrix, variations in the X-ray tube emission, evaporation and density changes of the sample and interference by Fe. As little as 3 g of sample, containing a few p.p.m. of Ni, can be used and the close correlation between the results obtained by this and other methods indicates that the procedure is accurate and precise. For duplicate determinations the precision is within 0.6% and the accuracy is within 3%, approaching 1% when little Fe is present in the sample. K. A. PROCTOR

155. Determination of aluminium and titanium in heat-resistant nickel-chromium (80:20) refractory alloys. V. Duriez and J. Barboni. *Rev. Nickel*, 1958, 24, 11-16.—The alloy is dissolved with H_2SO_4 and H_2O_2 . Electrolysis with a mercury electrode separates Fe, Cr, Cu, Co, Mo, Mn and most of the Ni; Al, Ti and some Ni remain in solution. The Ni is pptd. with dimethylglyoxime and removed by filtration. The soln. is made strongly acid with HCl and the Ti is pptd. with aq. cupferron soln. The Al in the filtered soln. is pptd. with quinoline in acetic acid, the ppt. is calcined and the Al is weighed. The Ti-containing ppt. is calcined and the Ti is converted into perititanic acid and determined by colorimetry. This method is simple, rapid and accurate, as shown by the percentage recovery of known amounts of added Al and Ti. The analytical methods used to determine the amounts of C, Si, Fe, Cr, Mn, Mo, Co and Ni in the alloy are discussed. CHEM. ABSTR.

156. Chemical microscopy of isoquinoline. Identification of the noble metals. H. F. Schaeffer (Emporia Coll., Kans., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1111-1112.—From 5 to 50 μg of Au, Pt, Pd, Ir or Ru in one drop of soln. can be detected by the characteristic micro-crystalline ppt. formed on the addition of one drop of a 0.4 *M* soln. of

isoquinoline in *N* HCl, or of a mixture of this soln. with an equal vol. of 0.8 *M* aq. NH_4SCN . The colours and shapes of the crystals and the limits of sensitivity are given. Osmium neither interferes nor yields crystals; Rh reduces the sensitivity when Pt or Pd is present.

W. J. BAKER

157. Spectrophotometric determination of palladium. III. A comparative study of 2-mercaptobenzothiazole and 2-mercaptobenzimidazole as analytical reagents. A. K. Majumdar and M. M. Chakrabarty (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1959, 20 (4), 379-385.—The reagents are interchangeable in the following method. *Procedure*.—To the soln. of Pd^{2+} add 2 ml of a 0.2% soln. of the reagent in dil. aq. alkali, add 2.5 ml of ethanol and adjust the total vol. to 25 ml and the pH to between 3 and 6.5. Determine the extinction at 380 $\text{m}\mu$ in a 1-cm cell and correct for a reagent blank. Beer's law is followed at concn. of Pd from 0.4 to 6 μg per ml, and minimum errors are obtained at 1.6 to 4.0 μg of Pd per ml. The ratio of metal to reagent in the complexes is 1:2 and the dissociation const. are $\approx 10^{-12}$. H. N. S.

158. Amperometric estimation of palladium. A. K. Majumdar and M. M. Chakrabarty (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1959, 20 (4), 386-389.—Polarographic diffusion currents are plotted for Pd^{2+} , bismuthiol I (I), bismuthiol II (II), 2-mercaptobenzothiazole (III) and 2-mercaptobenzimidazole (IV) in soln. buffered with Na acetate-acetic acid soln. (27.2 g of cryst. Na acetate and 11.6 ml of glacial acetic acid diluted to 100 ml with H_2O). I is used for the amperometric titration of Pd^{2+} at an applied potential of -0.3 V vs. the S.C.E.; II, III and IV are used at -0.5 V. All the reagents yield satisfactory results for 1.2- and 2.8-mg quantities of Pd, but I and III give erroneous results in the titration of 6 mg of Pd. H. N. S.

159. Quick and precise heterometric micro-determination of traces of palladium in metals with nitron. M. Bobtelsky and J. Eisenstadter (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1959, 20 (4), 352-357.—The heterometric titration of Pd^{2+} (≈ 0.5 mg) in thiocyanate soln. (cf. *Anal. Chim. Acta*, 1959, 20, 216) is carried out with errors of $< 1\%$ in the presence of 21 other metals, generally in large excess. No masking agent is necessary for Ca^{2+} , Ba^{2+} and Mg^{2+} ; triphosphate is used for Cd^{2+} , Pb^{2+} and Ti^{4+} , and citrate for Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Fe^{2+} , Cr^{3+} , Al^{3+} , UO_2^{2+} , Sb^{3+} , Bi^{3+} , Cu^{2+} , Hg^{2+} , Th^{4+} , Ce^{3+} and ZrO^{2+} , but the titration fails in the presence of KCN, NH_3 or the tetrasodium salt of EDTA. H. N. S.

160. Micro-crystalline test for osmium. H. F. Schaeffer (Emporia Coll., Kans., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1112-1113.—When one drop of a 3% soln. of 1:2:3:4-tetrahydro-6-methoxyquinoline in 2 *N* HCl is added to one drop (≈ 75 μg of Os) of a dil. soln. of OsO_4 (0.2 to 1%), deep red-green dichroic crystals are formed within a few minutes and can be identified at a magnification of 50 to 100. Gold and Pt interfere, but Cu and Ir do not. Osmium in low concn. (≈ 20 μg) is volatilised from a micro-beaker on to a hanging drop of the reagent on a slide. W. J. BAKER

161. New spectrophotometric procedure for platinum with tin(II) chloride. S. S. Berman and E. C. Goodhue (National Res. Council, Ottawa, Canada). *Canad. J. Chem.*, 1959, 37 (2), 370-374.—The

procedure described, by means of an absorption peak at 310 μ , can be used for determining Pt concn. of 0.4 to 6 p.p.m. in fumed H_2SO_4 or HNO_3 soln. Several factors affecting the intensity and stability of the absorbing complex have been investigated. The mean deviation of the absorbances of a soln. containing 2 p.p.m. of Pt was 0.5% (12 determinations). Palladium and Rh interfere, but Cu, Ni, Fe and Cr, up to 50 times the amount of Pt, produce a max. error of 3%.

K. A. PROCTOR

162. Reconnaissance observations on the combined use of ion-exchange enrichment and spectrochemical analysis for the determination of trace constituents in silicate rocks. R. A. Edge, R. R. Brooks, L. H. Ahrens and S. Amdur (Dept. of Chem., Univ. of Cape Town, S. Africa). *Geochim. et Cosmoch. Acta*, 1959, 15 (4), 337-341.—A reconnaissance investigation into the combined use of cation- and anion-exchange enrichment and spectrographic analysis for the determination of Ag, Be, Bi, Cd, Cs, In, La, Mo, Nb, Sn, Pb, Tl, Y and Zn in silicate rocks and allied materials indicates that many of these elements could be easily detected in a wide variety of rocks and soils. The scope of the combined procedure seems likely to be very wide, and it is evidently possible to determine several elements in a single operation. Brief details are given of the procedure followed. R. A. HOWIE

163. Micro-analysis of silicate and carbonate minerals. I. Determination of ferrous iron. J. P. Riley and H. P. Williams (Oceanography Dept., Univ., Liverpool). *Mikrochim. Acta*, 1959, (4), 516-524 (in English).—Procedure—The sample (3 to 5 mg), previously dried at 110°, is weighed into a Teflon tube, and is shaken with a few drops of N-saturated acid mixture (HF -50% H_2SO_4) (1:9) to give a suspension. The tube is then filled with acid mixture, stoppered, well shaken and immersed for half its length in a boiling-water bath for 40 min. When cool, the contents of the tube are treated with 5 ml of 2:2'-dipyridyl soln. (0.2% in 0.2 N HCl) and 20 ml of 2 M Na acetate. After dilution to 100 ml (250 ml if >20% of FeO is present in the sample), the extinction of the soln. is measured against a reagent blank at 522 μ . Ferric iron does not appear to interfere, but large amounts of S^{2-} may cause interference by reducing some Fe^{III} . Good agreement with results by other methods is found for samples with a FeO content ranging from 0.3% to 28%. Standard deviations of ± 0.07 and ± 0.03 are found for FeO contents of $\approx 9\%$ and $\approx 2.3\%$, respectively.

II. Determination of water and carbon dioxide. J. P. Riley and H. P. Williams. *Ibid.*, 1959, (4), 525-535 (in English).—The apparatus is similar to that used for determinations of C and H. The sample (10 mg) is ignited in the tube-furnace at 1100° to 1200° in an atmosphere of purified N. The CO_2 is absorbed in a tube packed with soda asbestos and $\text{Mg}(\text{ClO}_4)_2$, and the H_2O in one packed with $\text{Mg}(\text{ClO}_4)_2$ and a P_2O_5 -pumice mixture. The procedure has been applied successfully to the analysis of both carbonates and silicates; sulphide S causes no interference. For a sample with 4.1% of H_2O and 0.2% of CO_2 , standard deviations are ± 0.05 and ± 0.14 , respectively. It is estimated that 7 or 8 determinations could be performed in an 8-hr. working day. J. H. WATON

See also Abstracts—4, Titration of Mg, Ca, Mn and Ni. 6, Titration of halogens, isocyanide and Ag.

9, Radiometric titration of Zn, Pb and Ag. 10, Determination of Fe^{2+} . 12, Purity of powdered Cd, Cu, Zn and Fe. 194, Trace elements in coal. 205, Determination of Hg in urine. 288, Determination of NO_3^- . 289, Radio-assay of U and Pu. 292, Determination of trace components in gases. 314, Emission spectra of rare-earth and transuranic elements. 322, Determination of Cu, Pb, Cd and Zn. 328, Small amounts of H_2O in fluids.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives.

164. Quantitative infra-red analysis from published data. J. A. Perry (Res. Dept., Standard Oil Co., Whiting, Ind., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1054-1055.—Synthetic mixtures have been used to demonstrate that published i.r. absorption spectra and absorptivity data can be used for quant. analysis. Analytical results based on experimental absorptivity data do not differ appreciably from those based on published data. K. A. PROCTOR

165. Quantitative infra-red spectral analysis of solid organic compounds. K. Heller and U. Wagner (VEB Jenapharm, Jena). *Z. anal. Chem.*, 1959, 167 (2), 90-95.—In place of the usual methods of preparing solid compounds for i.r. analysis, the compound is melted between two plates of rock-salt or potassium bromide, approx. 5 cm by 2 cm by 0.8 cm thick, divided by transverse grooves into four similar areas. The two end areas have aluminium foil sandwiched between them which determines the thickness of the sample. The two middle areas contain, respectively, the sample and a reference compound, or one area may be left empty. The sample is introduced by carefully warming the plates, which are clamped together with a little of the solid compound on the edge. Capillary attraction draws the molten sample into the space between the plates where, on removing the source of heat, it solidifies into a clear homogeneous film. Typical analyses for cholane and pregnane derivatives are quoted to illustrate the use of the technique. H. M.

166. Concentration of impurities from organic compounds by progressive freezing. J. S. Matthews and N. O. Coggeshall (Gulf Research and Devel. Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1124-1125.—Several variables in the application of this method have been studied, viz, the effect of stirring, the speed of lowering the sample tube into the cooling bath, the temp. of cooling, the size of the fraction removed, and the effect of impurity concn. on the efficiency of separation of the impurities. K. A. PROCTOR

167. Simple rapid Dumas method for the micro-determination of nitrogen. K. Eder (Éc. de Chim., Univ. Genève, Switzerland). *Mikrochim. Acta*, 1959, (4), 631-634 (in German).—The Dumas-Pregl procedure can be carried out much more rapidly by the use of a modification in the combustion technique. Results are accurate to within $\pm 0.5\%$ (11 analyses). G. P. COOK

168. Can the acid-containing receiver in the Kjeldahl distillation be replaced by one charged with boiled water? E. Schulek, K. Burger and M. Fehér (L. Eötvös Univ., Budapest). *Z. anal. Chem.*, 1959, **167** (1), 28-31.—From experimental data on the partial pressures of NH_3 above aq. soln. of various concn. it is concluded that only a very small amount of NH_3 is likely to be carried over during the removal of excess of H_2SO_4 from a Kjeldahl digestion mixture by evaporation in a stream of air or inert gas, even if the residue is <1 ml. A maximum error of 0.05 to 0.08% might be introduced, but this can be eliminated by the use as a receiver of a 100-ml flask, containing 20 to 30 ml of freshly boiled and cooled water. The condenser tube dips into the water and, during distillation, exchange between the air inside and that outside the flask is prevented by a plug of cotton wool. Results obtained with such a receiver are tabulated.

S. M. MARSH

169. Micro-determination of sulphur in organic compounds by absorption with silver. Takeo Sudo, Daizo Shimoe, Takatomo Tsuji and Yukiko Soeda (Kurosaki Fac., Mitsubishi Chem. Ind., Yawata, Fukuoka-ken). *Japan Analyst*, 1959, **8** (1), 42-48.—Electrolytic silver wool (cf. Mitsui and Sato, *Mikrochim. Acta*, 1956, 1603) is used for the absorption of SO_2 . By the use of 2 g of silver wool, the absorption is complete at 420° in a current of O (10 ml per min.), the coeff. of variation being $\approx 0.1\%$. The Ag_2SO_3 is extracted with water at 90° , the soln. is acidified with 2 ml of 4 N HNO_3 , and the Ag is titrated with 0.01 N NH_4SCN by the Volhard method. This method is applicable to S as a micro-component or to liquid samples if the technique of Gouverneur and van Dijk (*Anal. Chim. Acta*, 1953, **9**, 59) is used.

K. SAITO

170. The rapid micro-analytical determination of elements in organic substances by the flask method. II. Determination of arsenic. W. Merz (Badischen Anilin- & Soda-Fabrik A.-G., Ludwigshafen/Rhein, Germany). *Mikrochim. Acta*, 1959, (4), 640-646.—The sample is burned in an Erlenmeyer flask filled with O and the combustion products are absorbed in dil. iodine soln. in which As^{III} is oxidised to As^{V} . The As is determined by the molybdoarsenate blue reaction, with hydrazine sulphate as reductant; the excess of iodine from the absorber does not interfere. Concn. of As >10 μg are measured on a filter photometer and those of <10 μg with a spectrophotometer. The mean error for a single determination is $\pm 0.2\%$.

G. P. COOK

171. Automatic coulometric micro-determination of unsaturation with kinetic proof of real equivalence-point. W. Walisch and M. R. F. Ashworth (Inst. Organ. Chem., Univ. of the Saar, Saarbrücken, Germany). *Mikrochim. Acta*, 1959, (4), 497-504 (in English).—Bromine is generated by the electrolysis of NaBr and the amount consumed is measured by normal coulometric means. The method is specially suitable for mono-olefinic hydrocarbons, giving a reproducibility of $\pm 0.3\%$. The apparatus is fully automatic, and with brominations of low reaction rate (which give intermittent electrolysis and consumption of bromine) a stopwatch, which is coupled to the apparatus, records the aggregate time of electrolysis. Mixtures can be analysed when the olefin components are brominated at sufficiently different speeds. It is possible to determine, by kinetic measurements, according

to the Guggenheim procedure for first-order reactions, whether the addition reaction is complete and unaccompanied by side-reactions.

G. P. COOK

172. Solubilisation chromatography. III. Ethers, carboxylic acids and hydrocarbons. J. Sherma and W. Rieman, III (State Univ., New Brunswick, N.J., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (4), 357-365.—Mixtures of aliphatic and aromatic ethers, saturated fatty acids and substituted benzenes and naphthalenes are separated by elution through columns of ion-exchange resins with aq. soln. of acetic acid as eluents. The theory of solubilisation chromatography (cf. *Ibid.*, 1958, **18**, 214; 1958, **19**, 134) is discussed in the light of these experiments.

H. N. S.

173. Quantitative gas chromatography of reaction products from the catalytic oxidation of ethylene. C. H. Amberg, E. Echigoya and D. Kulawic (Div. of Appl. Chem., Nat. Res. Council, Ottawa). *Canad. J. Chem.*, 1959, **37** (4), 708-713.—For the routine analysis of ethylene oxidation products, a two-stage gas-chromatographic technique permits determination of ethylene oxide, CO_2 and ethylene in a 10-ml sample of moist air. The two columns (in a bath at $30^\circ \pm 0.05^\circ$) are usable in series or in parallel. Percolates (He carrier at 31 p.s.i.g., issuing at 90 ml per min.) are analysed by one thermal-conductivity cell. The columns are packed with *n*-octadecane-Celite 545 (2:5, by wt.) and with silica gel, respectively. The sample is introduced into the columns arranged in series; after 5-6 min. they are switched to parallel flow. Ethylene oxide and water (neither may enter the silica gel) are still on the Celite, and CO_2 and ethylene have passed through this on to the silica gel. The apparatus, after calibration, is at least as accurate as the measuring out of synthetic ternary mixtures used for testing the apparatus (to within $\pm 5\%$ and $\pm 2\%$ for gas concn. in the 0.3% and 1.0% region, respectively). The results are highly reproducible.

J. P. STERN

174. Analysis of C_5 to C_8 saturated hydrocarbons by gas-liquid chromatography. Lu-Pin Cheng and Yin-Sheng Hsu. *Scientia, Peking*, 1958, (3), 89-90.—With diatomaceous earth (73 g) containing 19.8% of benzophenone as stationary phase and H as carrier gas, a mixture of C_5 to C_8 saturated hydrocarbons (0.02 ml) at 52° was separated into peaks of the following relative limiting retention vol.: pentane 1.0; isopentane 0.76; 2,2-dimethylbutane 1.27; 2-methylpentane 1.86; 2,3-dimethylbutane (I) 1.86; 3-methylpentane (II) 2.19; cyclopentane (III) 2.60; hexane (IV) 2.60; methylcyclopentane 4.54; cyclohexane 6.39. The accuracy was 1%. Complete separation of components was achieved by distillation before chromatography and dividing the mixture at b.p. 58° . I and III were thus separated from II and IV.

CHEM. ABSTR.

175. Iodimetric determination of the reducing capacity of aluminium alkyls. S. A. Bartkiewicz and J. W. Robinson (Esso Res. Lab., Baton Rouge, La., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (4), 326-329.—Details are given of a glass "bomb" that can be flushed with N and which enables a sample of aluminium alkyl to be weighed into the titration beaker through a capillary delivery-tip. The sample is delivered below the surface of a measured vol. of a standard soln. of iodine in benzene, containing 2 g of KI, the beaker being suitably covered

and flushed with N. Acetic acid is then added to the reaction mixture and the excess of iodine is titrated with 0.2 N $\text{Na}_2\text{S}_2\text{O}_3$. This procedure does not enable aluminium alkyls, alkoxides and hydrides to be differentiated. H. N. S.

176. **Infra-red spectra of 1:2-epoxybutane.** R. A. G. Carrington (Shell Res., Ltd., Chester, England). *Anal. Chem.*, 1959, **31** (6), 1117.—The spectrum of a synthetic sample of 1:2-epoxybutane was recorded on a Grubb Parsons prism spectrometer (S4), using an undiluted sample and cells of 50 μ and capillary path length. The spectrum has 2 strong bands at 11.1 and 12 μ . K. A. PROCTOR

177. **Separation of aliphatic alcohols and hydrocarbons by extraction.** V. B. Kozan, V. M. Fridman and T. G. Romanova. *Zhur. Prikl. Khim.*, 1959, **32** (4), 847-852.—Mixtures of aliphatic alcohols and of hydrocarbons can be completely separated by extraction for 0.5 hr., either once with a 2 to 3-fold amount of ethanediol or twice with an equal amount, the individual layers then separate out rapidly and completely. Practically pure hydrocarbon is obtained by decanting the upper layer, and alcohols can be recovered from the lower layer by simple rectification. Aq. soln. of the solvent can also be used for the extraction. K. R. C.

178. **Turbidimetric micro-method for analysis of tert.-butyl alcohol.** M. R. F. Ashworth (Inst. Organ. Chem., Saar Univ., Saarbrücken, Germany). *Mikrochim. Acta*, 1959, (4), 506-512 (in English).—The method is based on the turbidity produced by tert.-butyl alcohol with a HgSO_4 - H_2SO_4 reagent similar to the Deniges reagent for the qual. testing of tertiary alcohols. The effects of the concn. of H_2SO_4 , Hg and tert.-butyl alcohol, temp. and light were studied. Concn. as low as 1 to 6 mg per litre can be determined with an error <5%. G. P. COOK

179. **Determination of purity and assay of sodium lauryl sulphate.** P. Schaller (Pharm. Inst. der ETH, Zürich, Switzerland). *Pharm. Acta Helv.*, 1959, **34** (4), 204-213.—Purity tests and a method of assay for sodium lauryl sulphate (I) in the pure compound and in preparations are given. The tests for purity include those for identification, alkalinity, NaCl, Na_2SO_4 , free alcohol, total alcohol and solubility according to the standards laid down by U.S.P. XV. The assay of I is based on the method of Wickbold (*Fette u. Seif.*, 1952, **54**, 394). I is quant. pptd. in aq. soln. by p-toluidine, the ppt. is extracted into diethyl ether, and is titrated in an ethanol medium with standard NaOH soln. to cresol red indicator. The pH of pptn. should not exceed 3.0 and a three-fold excess of the reagent is necessary. Quantities as little as 0.2 g can be determined with an error $\pm 2\%$, and a mean recovery of 99-86% was obtained for specially purified I; the mean equiv. wt. for this purified substance was found to be 305.5. G. P. COOK

180. **Absorption spectra of formic acid and its methyl ester in the infra-red region.** V. Lorenzelli and K. D. Möller (Lab. Res. Phys., Sorbonne, Paris). *Compt. Rend.*, 1959, **249** (4), 520-522.—The i.r. absorption spectra between 14 and 50 μ of formic acid and methyl formate in the vapour state have been determined. N. E.

181. **Quantitative determination of bromoacetic acid and its derivatives.** K. Woidich, L. Schmid,

T. Langer, H. Gnauer and H. Woidich (Lebensmittelforschungsanst. u. dem II Chem. Univ.-inst., Wien, Austria). *Z. Lebensmittelforsch.*, 1959, **109** (4), 329-335.—A specific method for the quant. determination of bromoacetic acid (I) and its esters is based on the conversion of I into glycine and colorimetric measurement of the glycine (after isolation) with ninhydrin and Cd acetate. The sample of fruit juice, wine or beer is extracted with diethyl ether, and the ether phase is shaken with conc. aq. NH_3 at room temp., which results in (i) the exchange of Br for an $-\text{NH}_2$ group and (ii) the saponification of the ester. After evaporation of the ether, the aq. glycine is either purified by treatment with active carbon or by paper chromatography. Recent methods for determining organically bound Br were examined and the Kolthoff titration process as modified by Kainz (cf. *Brit. Abstr. C*, 1951, 368) is recommended. The saponification of bromoacetic ester and the stability of KBr at 450° to 500° are discussed. S.C.I. ABSTR.

182. **Determination of acetic anhydride by a rapid thermometric method.** E. Angelescu and N. Bărbulescu (Univ., Bucharest, Romania). *An. Univ. "C. I. Parhon" București, Ser. Stiinț. Nat.*, 1957, (13), 93-100.—The method of Richmond and Eggleston, based on the temp. increase when aniline is acetylated, is modified so that more rapid results can be obtained in the determination of acetic anhydride in the presence of acetic acid. To a test-tube used for the freezing-point determination, to which a Beckmann thermometer and stirrer are fitted, add 10 ml of a 20% soln. of aniline in toluene, and after thermal equilibrium has been attained add 1 ml of the acetic anhydride soln. The max. temp. obtained is noted and the quantity of acetic anhydride is calculated from the formula $C = Kt$, where C is the percentage of acetic anhydride, t is the increase in temp. due to the acetylation of aniline, and K is the experimental constant which represents the percentage of acetic anhydride necessary to increase the temp. by 1°; K can be determined for a given apparatus with pure acetic anhydride and with known mixtures of acetic anhydride and acetic acid. The error is $\pm 1.2\%$. CHEM. ABSTR.

183. **Detection of sorbic acid.** H. Böhme and L. Bertling (Inst. f. Pharm. Chem. u. Lebensmittelforsch., Univ., Marburg/Lahn, Germany). *Z. Lebensmittelforsch.*, 1959, **109** (4), 336-337.—Sorbic acid is separated as the difficultly soluble mercurous salt; after the addition of HCl, evaporation, and micro-sublimation at 90° to 100°, the free sorbic acid is identified by its m.p. (134° to 135°) and eutectic temp. with benzanilide (123°) or phenacetin (107° to 108°). S.C.I. ABSTR.

184. **Identification of 2-ethylhexyl hydrogen sebacate in di-(2-ethylhexyl) sebacate.** E. B. Dismukes (S. Res. Inst., Birmingham, Ala., U.S.A.). *J. Amer. Oil Chem. Soc.*, 1959, **36** (4), 154-155.—To identify 2-ethylhexyl hydrogen sebacate (I) in degraded di-(2-ethylhexyl) sebacate oils (i.e., oils that have become oxidised and pyrolysed in high-temp. lubrication), the oil (15 g) is dissolved in 45 ml of a mixture of vinyl cyanide and methanol (2:1, by vol.) (II); the soln. is extracted with 180 ml of Skellysolve C (III) and the III phase is discarded; the II phase is again extracted with a fourfold excess of III, the extraction being repeated if the sample contains <5 moles % of I; the residual II

phase is then evaporated, and the residue is dissolved in **III**. The soln. (concn. 0.1 g per ml) is examined in the range 1600 to 2000 cm^{-1} ; **I** has absorption peaks at 1710 and 1740 cm^{-1} .

H. L. WHITEHEAD

185. Infra-red absorption and Raman spectra of diphenyl. A. Hidalgo (Inst. Optica "Daza de Valdés," Madrid). *An. Real Soc. Fis. Quim.*, **B**, 1958, **54** (6), 451-458.—Detailed spectra are given.

N. E.

186. The colour reactions of certain polyhydric phenols with *p*-dimethylaminobenzaldehyde. J. Kolšek and M. Perpar (Inst. f. org. Chem., Univ. Ljubljana, Yugoslavia). *Z. anal. Chem.*, 1959, **187** (3), 161-164.—A quant. method for determining resorcinol (**I**) or phloroglucinol (**II**) with *p*-dimethylaminobenzaldehyde (**III**) is described; ethanol and H_2O are used as solvents. The colour given by **I** with **III** is unstable; the absorption max. changes slowly from 518 $\text{m}\mu$ to 560 $\text{m}\mu$, but is independent of temp. or the ratio of **I** to **III**. Beer's law is followed for concn. of $> 5 \mu\text{g}$ of **I** per ml. **II** with **III** gives a red colour, the max. intensity of which is attained after 1 hr. The absorption max. is constant at 550 $\text{m}\mu$ and is independent of temp. or the ratio of **II** to **III**; Beer's law is followed for concn. of $> 200 \mu\text{g}$ of **II** per ml. *Procedure*—Add 2 ml of reagent (0.5 g of **III** in a mixture of 8.5 g of conc. H_2SO_4 and 8.5 ml of H_2O) to 2 ml of the phenol soln. and measure the extinction at 518 $\text{m}\mu$ after 30 min. for **I**. For **II**, proceed as for **I**, but measure the extinction at 550 $\text{m}\mu$ after 20 min.

P. D. PARR-RICHARD

187. Precise determination of the molecular weight of trinitrobenzene complexes. J. C. Godfrey (Sch. of Chem., Rutgers, State Univ. of New Jersey, New Brunswick, U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1087-1089.—The method depends on the conversion of the complex into a highly coloured compound with an excess of K ethoxide and the measurement of its extinction at 502 $\text{m}\mu$. Values obtained are usually within $\pm 0.5\%$ of the mol. wt. of the complex. The instability of certain organic trinitrobenzene complexes is a common source of error.

K. A. PROCTOR

188. Extraction analysis of nitrobenzoic acid. H. Buchowski and Z. Olempska (Polish Acad. Sci., Warsaw). *Chem. Anal.*, Warsaw, 1958, **3** (3-4), 635-640.—A mixture of *o*- and *p*-nitrobenzoic acids is analysed polarographically before and after extraction with a mixture of diethyl ether and toluene (3:1) at pH 4.2 (0.3 *M* acetate buffer). All measurements are made at $20^\circ \pm 0.5^\circ$. From the results the relative content of each isomer can be calculated.

H. DMOWSKA

189. Studies in bivalent chromium salts. VIII. Estimation of nitro, nitroso and azo compounds, quinones and carbohydrates with chromous sulphate. J. P. Tandon (Chem. Lab., Balwant Rajput College, Agra Univ., India). *Z. anal. Chem.*, 1959, **187** (3), 184-192 (in English).—The direct titration of organic compounds with the use of visual indicators is described. For nitro, nitroso or quinonoid compounds, CO_2 is passed into the soln., which is then titrated with CrSO_4 with neutral red or phenosafranin as indicator. Alternatively, an excess of CrSO_4 soln. is added and the excess is back-titrated with a ferric soln., with NH_4SCN as indicator. For picric acid or *p*-nitrobenzaldehyde, a little

conc. HCl should first be added. Azo dyes, after saturation with CO_2 , can be titrated with CrSO_4 or TiCl_3 soln., giving green and colourless end-points, respectively. In the reduction of tartrazine, 6 *N* HCl is added and the soln. is heated before titrating. When TiCl_3 is used, tartrate must be added. In the reduction of Congo red, tartrate should be present even when CrSO_4 is used as titrant. *Procedure for carbohydrates*—Mix 100 ml of Fehling's soln. **I** with 75 to 100 ml of Fehling's soln. **II** and boil; slowly add 50 ml of 0.5 to 1% test soln., then 100 ml of cold H_2O . Filter, acidify the filtrate with HCl and make up to 500 ml. To a 50-ml aliquot add 25 ml of conc. HCl and a little indicator. Pass CO_2 for 5 min. and titrate slowly with CrSO_4 soln.

P. D. PARR-RICHARD

190. Infra-red and Raman spectra of isoxazole: the vibrational assignment. S. Califano, F. Piacenti and G. Speroni (Ist. Chim., Napoli, Italy). *Spectrochim. Acta*, 1959, (2), 86-94.—The i.r. and Raman spectra of the isoxazole molecule have been measured over the range 300 to 3200 cm^{-1} in the liquid and vapour phases. By comparison with the similar spectra of furan and pyrrole, assignments of which have been established by other workers, and by inspection of the rotational envelope of the vapour bands, a reasoned assignment has been made.

P. T. BEALE

191. Infra-red spectra of pyrazine- and pyridine-carboxylic acids and their derivatives. Shigeru Yoshida and Motoji Asai (Takamine Res. Lab., Sankyo Co., Nishi-Shinagawa, Shinagawa-ku, Tokyo). *Chem. Pharm. Bull.*, Japan, 1959, **7** (2) 162-171.—Data are recorded for pyrazinic acid, pyrazinedicarboxylic acid and its mono-ethyl ester, picolinic, nicotinic and isonicotinic acids, and for the 2-chloro- and 5 other derivatives of isonicotinic acid. The acids were deuterated and the shifts of absorption were examined.

N. E.

192. Infra-red spectra of methyl- and silyl-phosphines. H. R. Linton and E. R. Nixon (Dept. of Chem., Univ. of Pennsylvania, Philadelphia, U.S.A.). *Spectrochim. Acta*, 1959, (2), 146-155.—The i.r. spectra of methyl- and silyl-phosphines in the gas phase, over the range 300 to 4000 cm^{-1} , have been recorded. Vibrational assignments have been made on the basis of a C_s model, and a complex absorption from 400 to 500 cm^{-1} in silyl phosphine suggests that the overtone of the internal torsion may lie in this region.

P. T. BEALE

193. Automatic titration of peroxides in petroleum products. J. S. Matthews and J. F. Patchan (Gulf Res. & Devel. Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1003-1005.—The de-aerated sample is allowed to react with a soln. of KI (15 g) in water (10 ml), isopropyl alcohol (100 ml) and glacial acetic acid (1 ml) and the liberated iodine is immediately and continuously reduced to iodide, as it forms, by the automatic addition of standard $\text{Na}_2\text{S}_2\text{O}_3$ soln., the end-point being determined potentiometrically. The automatic titrator is set at -50 mV , and the concn. of iodine is rarely allowed to exceed a very small value. The method is applicable to hydroperoxides and diacyl peroxides in low or high concn. For peroxide values > 1 the accuracy is within 3%, and is within 0.1 peroxide value for lower values. Petroleum distillates, charge stocks, fuels, propylene polymers, keto alcohols and aldehydes can be analysed by this method.

W. J. BAKER

194. Trace elements in coal and their spectrographic determination. W. Radmacher and H. Hessler (Brennstoffchem. Inst. der Ruhrkohlen-Beratung G.m.b.H., Essen). *Z. anal. Chem.*, 1959, **167** (3), 172-182.—When ashing solid fuels for analysis, the ashing temp. should be relatively low and a reducing atmosphere avoided. For qual. analysis, the ash is mixed with NH_4Cl and graphite (2:1:1) and placed in the cup of a carbon electrode. For high sensitivity, 8-amp. d.c. continuous arc excitation is used. For semi-quant. work, interrupted arc excitation is suitable. The samples of ash- NH_4Cl -graphite are mixed with In_2O_3 as internal standard. For quant. analysis the following procedure is employed (also suitable for clinker). Ash (400 mg) is mixed with borax (1000 mg) and In_2O_3 (30 mg) and heated in a platinum crucible to give a clear melt. When cool, this is mixed with graphite (1:1.5) and pressed into electrode form. An iron spectrum is also recorded for comparative purposes. The sources of error in the procedure are discussed, and the reproducibility for different elements is given. P. D. PARR-RICHARD

195. Identification of anionic surface-active agents by infra-red absorption of the barium salts. J. W. Jenkins and K. O. Kellenbach (Res. & Devel. Dept., Colgate Palmolive Co., Hudson St., Jersey City, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1056-1059.—Organic sulphates and sulphonates in detergents can be removed and identified by extraction with ethanol, followed, after removal of soap or free fatty acid by acidification and extraction, by pptn. of the barium salts, which are insol. in H_2O and hydrocarbons. The i.r. spectrum of the dried ppt. is compared with those of known compounds, and the mol. wt. of the original surfactant can be determined by igniting the ppt. to BaSO_4 . The i.r. spectra of 10 pure organic sulphates and sulphonates are shown. W. J. BAKER

196. Potentiometric estimation of carbonyls in Indian vetiver oils. I. C. Nigam, D. R. Dhingra and G. N. Gupta (H.B. Technol. Inst., Kanpur, India). *Perfum. Essent. Oil Rev.*, 1959, **50** (4), 297-299.—The carbonyl content of dark oils such as Indian vetiver oil cannot be determined by conventional colorimetric methods. Potentiometric titration to pH 3.5 after reaction with a standardised hydroxyammonium chloride soln. for 24 hr. at room temp. is recommended. The colorimetric method of Zutshi and Sadgopal (*I.S.I. Bull.* 8, 1956, No. 5) gives higher results owing to differences in the pH of the visual end-point. H. B. HEATH

197. Determination of sugars in sulphite waste liquor. B. Pszonka and K. Sarnecki (Pulp and Paper Res. Inst., Łódź, Poland). *Chem. Anal.*, *Warsaw*, 1958, **3** (3-4), 699-702.—The concn. of hexoses is calculated from the difference in reducing power before and after fermentation. The concn. of pentoses is determined titrimetrically with furfuraldehyde. H. DMOWSKA

198. Determination of β - and γ -cellulose in rayon cellulose pulps. W. Piela, T. Podgódek and A. Winczakiewicz (Paper and Cellulose Inst., Łódź, Poland). *Chem. Anal.*, *Warsaw*, 1958, **3** (3-4), 693-697.—The Cross and Bevan method, the standard Swedish and Czech methods and a modified Swedish method are discussed and compared. Discrepancies in the results are caused by the different conditions of mercerisation. H. DMOWSKA

199. Determination of the resin content of phenolic resin mouldings. H. Wallhäuser (Kunststoffabt. d. Staatl. Materialprüfungsanst. Darmstadt). *Kunststoffe*, 1959, **49** (4), 171-173.—The acetone-extraction method for the determination of the resin content of novolak-based moulding powders cannot be used for resole-based powders on account of the hardening and insolubilisation of the resole at the extraction temperature. The use of cyclohexanone in place of acetone avoids this difficulty. The powder is extracted in a Soxhlet apparatus for 2 hr. (novolak) or 3 hr. (resole), followed by a 2-hr. extraction with methanol to remove retained cyclohexanone. A correction for the water formed must be made, derived from the water content (W) determined as the weight loss after 2 hr. at 105° ; this, for a novolak with a resin-containing filler = $(2W + 1)\%$; for a novolak with a non-resinous filler, $2W\%$; for a resole powder, $W\%$.

J. L. PROSSER

200. Determination of fumaric acid in polyesters. P. Fijolka and I. Lenz (Inst. für Kunststoffe d. Dtsch. Akad. der Wiss., Berlin). *Plaste u. Kautsch.*, 1959, **6** (1), 23-24.—Low values for the fumaric acid content of polyesters, determined by saponification and pptn. with HgNO_3 , may result from carrying out the pptn. in the presence of too high a concn. of HNO_3 or from washing the ppt. with hot aq. HNO_3 . Optimum results are obtained by pptn. with 5% aq. HgNO_3 in a 10 to 20% excess, in a medium of 3% HNO_3 , and washing the ppt. with cold 3% HNO_3 . L. A. O'NEILL

201. Determination of the metal contents of paint driers by flame photometry. P. J. Secrest (11541 S. Champlain Ave, Chicago). *Off. Dig. Fed. Paint Varn. Prod. Cl.*, 1958, **30**, 1026-1032.—A method for determining the metal content of calcium, cobalt, lead and manganese driers is described. The drier is dissolved directly in a benzene-acetone-alcohol solvent, and the metal concn. is obtained by comparing the emission of the soln. with that of a standard. Duplicate determinations require about 30 min. The coeff. of variation varies from $\pm 0.60\%$ for Pb to $\pm 0.85\%$ for Ca. Agreement with chemical methods is within 1%.

D. R. DUNCAN

202. Water determination in Freon-22 refrigerant by infra-red spectrophotometry. W. J. Diamond (Refrigeration Div., International Harvester Co., Evansville, Ind., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (3), 77-79.—The method of Benning *et al.* for the determination of the water content of Freon-12 (*cf. Anal. Chem.*, 1947, **19**, 867) has been modified for application to Freon-22. For routine testing a mixture of Freon-22 and Freon-12 (3:7) is prepared and the extinction at 2.67μ is determined with a 3-in. cell. This figure gives an apparent water content on the graph of water content of Freon-12 vs. extinction. From a calibration graph of the water equivalent of Freon-22 vs. the percentage of Freon-22 in the mixture, and a knowledge of the water content of the Freon-12 used to make the mixture, the water content of the Freon-22 can be calculated directly. Beer's law was obeyed for extinctions up to 0.7.

E. G. CUMMINS

See also Abstracts—17. Titration of metal acetates. 48. Assay of organic Hg compounds. 85. Determination of P in fuel ash. 87. Analysis of phosphate detergents. 122. Determination of chloramine T. 154. Determination of Ni in oils. 277.

Characterisation of fatty and other acids used in the soap industry. 281, Determination of methane in air. 295, Determination of carbonyl compounds.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

203. Influence of anions present in biological materials on the determination of sodium, potassium and calcium by flame photometry. J. Skarżyński, H. Panusz and J. Greger (Inst. of Physiol. Chem., Łódź, Poland). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 553-561.—The interference of PO_4^{3-} , SO_4^{2-} , NH_4^+ and HCO_3^- on the emission of K, Na and Ca is discussed. The inter-relationships are presented in the form of graphs. H. DMOWSKA

204. Determination of copper in blood serum with lead diethyldithiocarbamate. I. Dezső and T. Fülöp (Inst. of Med. Chem., Debrecen, Hungary). *Mikrochim. Acta*, 1959, (4), 592-595 (in German).—The serum (1 ml) is diluted to 6 ml with H_2O and is treated with 1 ml of 20% HCl. After 10 min., 2 ml of 20% trichloroacetic acid soln. is added and after a further 10 min. the soln. is filtered. To a 5-ml portion of the filtrate are added 1 ml of 2.5% aq. EDTA (disodium salt) soln. and a drop of 1% ethanolic *p*-nitrophenol soln. as indicator. After neutralisation with aq. NH_3 and H_2SO_4 , the soln. is extracted once with 5 ml of Pb diethyldithiocarbamate soln. in *n*-butanol (prep. described), and the colour is measured at 430 m μ . The recovery of Cu added to serum is generally >90% in the range from 0.5 to 2 μg per ml, and as little as 0.3 μg per ml can be determined. G. P. COOK

205. Micro-determination of mercury in urine. R. Fabre, R. Truhaut and C. Boudène. *Ann. Biol. Clin., Paris*, 1958, **16**, 286-298.—The organic matter in a 10-ml aliquot of urine is destroyed with H_2SO_4 and KMnO_4 in a specially designed flask. After the addition of hydroxyammonium chloride, urea, Na acetate buffer and oxalic acid to a pH of 1.5, the Hg is titrated with a soln. of a di- β -naphthylthiocarbazon in CHCl_3 . The technique is rapid, and as little as 4 μg of Hg per litre can be determined with an accuracy of 5%. The use of EDTA to prevent the interference of Cu, Au, Pd, Pt or Bi is discussed. CHEM. ABSTR.

206. Chemical testing procedures for the determination of ethyl alcohol. T. E. Friedemann and K. M. Dubowski (Fitzsimons Army Hosp., Denver, Colo.). *J. Amer. Med. Ass.*, 1959, **170** (1), 47-71.—This is a comprehensive review of methods for the determination of ethanol in tissues, body fluids and breath.

207. Simple method for detecting and determining ethanediol in body materials; analytical results in six fatal cases. R. N. Harger and R. B. Forney (Indiana Univ., Indianapolis). *J. Forensic Sci.*, 1959, **4**, 136-143.—Ethanediol (I) was determined in protein-free filtrates of blood or tissue homogenates by oxidising an aliquot of the filtrate with 0.1 *M* periodic acid. After 10 min. the formaldehyde formed was determined by adding a modified

Schiff reagent and reading the colour at 555 m μ against a water blank. If more than 30 μg of I is present in the aliquot used, the intense colour that results makes it necessary to dilute the original sample 2- or 3-fold. Urine can be diluted and analysed directly. Of blood samples taken from hospital patients (966 samples), 86% gave apparent concn. of I of up to 7 mg per 100 ml, and 97% of the results gave concn. of I of <16 mg per 100 ml. The highest value was 35 mg per 100 ml. Analyses of biological material obtained from 6 fatal cases are presented. CHEM. ABSTR.

208. Differential ultra-violet spectrophotometric determination of serum salicylates. L. A. Williams, R. A. Linn and B. Zak (Wayne County Medical Examiner's Office, Detroit, Mich., U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (1), 156-162.—Methods are described for the assay of salicylates in serum (1 ml for the macro- or 0.1 ml for the micro-method) depending on the difference in u.v. absorption at pH 13 and at pH 10.5. *Procedure*—To 1 ml of serum add 1 ml of 6 *N* HCl and 50 ml of CHCl_3 . Extract for 5 min. and then filter the CHCl_3 into a separating-funnel. Add 7 ml of 0.45 *N* NaOH to 45 ml or more of the CHCl_3 and extract for 3 min. Discard the CHCl_3 and centrifuge the aq. phase. Place 3 ml in each of two silica cells. To one cell add 0.5 ml of 0.45 *N* NaOH and to the other (for the reference soln.) add 0.5 ml of 16% NH_4Cl soln. Mix and record the difference spectrum on a ratio-recording spectrophotometer. The positive extinctions at approx. 246 and 316 m μ (max.) and the negative extinction at 280 m μ (min.) are proportional to salicylate concn. up to at least 50 mg per 100 ml of sample. Barbiturates, when present, can also be determined, whether or not salicylate is present. W. H. C. SHAW

209. Spectrophotometric determination of tolbutamide in plasma. T. Chulski (Upjohn Co., Kalamazoo, Mich., U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (3), 490-494.—The acidified plasma is extracted with CHCl_3 and, after removal of the CHCl_3 , is treated with 0.4% ethanolic (*p*-dimethylaminobenzaldehyde, and evaporated *in vacuo* to dryness. The residue is heated for 2.5 hr. at 70°, then cooled and dissolved in methanol, and the extinction is measured at 395 m μ . The method is satisfactory for plasma levels (30 to 200 μg per ml) after tolbutamide treatment, and gives a mean recovery of $100.4 \pm 5.2\%$. Normal plasma gives a blank value equiv. to $\approx 1 \mu\text{g}$ per ml.

W. H. C. SHAW

210. Determination of *N*-methyl-2-pyridone-5-carboxamide in urine. B. Gassmann and E. Scheunert (Nutrition Inst., Potsdam-Rehbrücke, Germany). *Int. Z. Vitaminforsch.*, 1958, **28**, 421-433.—*N*-Methyl-2-pyridone-5-carboxamide, the chief catabolic product of nicotinic acid in urine, is nitrated by means of KNO_3 dissolved in conc. H_2SO_4 , then extracted as the nitro compound with butanol, and determined photometrically. The sensitivity is 1.57×10^{-4} g per ml of urine. CHEM. ABSTR.

211. Colorimetric method for the measurement of the brain ammonia of the mouse: The effect of glutamine on the total measurable ammonia. D. G. Nathan and K. S. Warren (Nat. Inst. Health, Bethesda, Md., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **81** (2), 377-381.—The micro-diffusion ninhydrin colorimetric method described previously

(cf. Nathan and Rodkey, *Anal. Abstr.*, 1957, **4**, 4066) is adapted to the assay of NH_3 in brain tissue powdered at the temp. of liquid N. The mean concn. was 0.46 ± 0.035 mg per 100 g of tissue. The NH_3 evolved from glutamine under alkaline conditions was significant, but relatively constant. W. H. C. SHAW

212. Micro-estimation of succinate and the extinction coefficient of cytochrome c. V. Massey (Sheffield Univ., England). *Biochim. Biophys. Acta*, 1959, **34** (1), 255-256.—The method is based on the reduction by succinate in the presence of succinate dehydrogenase of phenazine methosulphate, which, in the reduced form, is then allowed to react with cytochrome c. Spectrophotometer cells are filled with a soln. (2-95 ml) containing phosphate, pH 7.6 (150 μmoles), cytochrome c (0-125 μmole), succinate (0 to 0-05 μmole) and succinic dehydrogenase (0-2 mg). The cells (together with a blank omitting the succinate) are incubated at 25° and the reaction is started by the addition of 0-05 ml of 0-01% phenazine methosulphate soln. (freshly diluted from 1% stock soln.). The extinction at 550 $\text{m}\mu$ is recorded until the difference between the blank and sample becomes constant. The calibration graph is rectilinear. W. H. C. SHAW

213. Determination of angiotensin [hypertension] in blood. A. C. Paladini, E. Braun-Menéndez, I. S. del Frade and Z. M. Marsani (Buenos Aires Univ., Argentina). *J. Lab. Clin. Med.*, 1959, **53** (2), 264-271.—A sensitive method for the isolation, assay and identification of angiotensin in 50 ml of blood is described. The sample is diluted with ethanol, and angiotensin in the filtrate is adsorbed on to Dowex 50-X2 resin. After elution with alkali the angiotensin is determined by pressor activity on intravenous injection into small rats. W. H. C. SHAW

214. Improvement of the method for determination of plasma and urine haemoglobin. T. R. Johnson (Walter Reed Army Med. Center, Washington, D.C., U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (3), 495-498.—A description is given of the construction and use of a special capillary pipette for measuring samples containing >400 mg of haemoglobin per 100 ml for subsequent determination by the benzidine method. Preliminary dilution of the sample is avoided. W. H. C. SHAW

215. Photometric determination of the sialic (N-acetylneuraminic) acid distribution in cerebrospinal fluid. A. Saifer and H. A. Siegel (Jewish Chronic Disease Hosp., Brooklyn, N.Y., U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (3), 474-483.—The method described is based on the reaction with diphenylamine in glacial acetic acid- H_2SO_4 at 100° and measurement of the extinction at 530 $\text{m}\mu$. Modifications for the determination of total, protein-bound and non-protein-bound sialic acid in 1-5 ml of cerebrospinal fluid are described. Results on samples from normal and diseased patients are given and their significance is discussed. W. H. C. SHAW

216. Identification of 2-hydroxystearic acid in spinal cord phrenosine by chromatographic separation of hydroxy fatty acids. V. P. Skipski, S. M. Arfin and M. M. Rapport (Sloan-Kettering Inst., New York, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **82** (2), 487-488.—Reversed-phase chromatography (Weiss, *J. Biol. Chem.*, 1956, **223**, 523) is

carried out with 65% or 95% acetic acid at 30° to 40° . With the 65% acid a good separation of 2-hydroxy-myristic, -palmitic, -stearic and -lignoceric acids is attained. The compounds are converted into bismuth salts and the Bi is detected as sulphide. W. H. C. SHAW

217. Acid fuchsin and uranyl nitrate in staining chromatograms of phosphatides. H. G. Bungenberg de Jong and G. R. van Someren (Univ., Leyden, Holland). *Proc. Kon. Ned. Akad. Wet., B*, 1959, **62** (3), 150-160 (in English).—Phosphatides having one positively and one negatively charged group in the molecule are most satisfactorily stained with a soln. of acid fuchsin (0-002%) and $\text{UO}_2(\text{NO}_3)_2$ (0-2%) in HCl (0-01 N). After being stained, the chromatograms are washed with 0-01 N HCl containing 0-2% of $\text{UO}_2(\text{NO}_3)_2$ and dried; red spots are obtained. In chromatograms of total egg-phosphatides, lecithin and cephalin and their lyso products, and sphingomyelin are detected by this means. Phosphatides containing one uncompensated group of acidic character in admixture with the above-mentioned type can be stained by including a basic dye (Brilliant green) in the staining soln. Soya-bean phosphatides, which are reported to contain both types, give red and green spots. Impurities in the chromatographic paper give rise to background coloration which cannot be completely avoided. The mechanism of the staining reaction is discussed. G. P. COOK

218. Histochemical identification of myelin phosphoglycerides by their ferric hydroxamates. C. W. M. Adams and A. N. Davison (Guy's Hospital Med. School, London). *J. Neurochem.*, 1959, **3** (4), 347-351.—The ferric hydroxamate reaction (Rapport and Alonzo, *J. Biol. Chem.*, 1955, **217**, 193) for the determination of phosphatides was adapted to the histochemical detection of phospholipid in myelin. Lipid smears or tissue sections were treated with alkaline hydroxylamine soln. for 20 min. After being rinsed in tap-water, the preparations were placed in acid FeCl_3 soln. for a further 20 min. Phosphoglycerides are the only naturally occurring tissue lipids that are stained when the reaction is applied in aq. as distinct from alcoholic soln. K. R. C.

219. Simplified spectrophotometric determination of ester groups in lipids. F. Snyder and N. Stephens (Oak Ridge Inst. Nuclear Studies, Tenn., U.S.A.). *Biochim. Biophys. Acta*, 1959, **34** (1), 244-245.—The adaptation of the ferric hydroxamate procedure described gives a rectilinear calibration graph up to 4 micro-equiv. of ester. *Reagents*—(A) Dissolve 5 g of ferric perchlorate (non-yellow) in 10 ml of 70% HClO_4 soln. and 10 ml of water. Dilute to 100 ml with cold abs. ethanol and store in a refrigerator. (B) Dilute 4 ml of A and 3 ml of 70% HClO_4 soln. to 100 ml with cold abs. ethanol. (C) Mix equal vol. of a soln. of hydroxylamine (2 g in 2-5 ml of water diluted to 50 ml with abs. ethanol) and 8% NaOH soln. (4 g dissolved in 2-5 ml of water and diluted to 50 ml with abs. ethanol). Centrifuge and decant the clear supernatant liquid for use. Prepare fresh daily. *Procedure*—Evaporate sample soln. in CHCl_3 to dryness under an i.r. lamp. Add 0-5 ml of acetone and dry again. To the residue add 1 ml of C and place in a water bath at 65° for 2 min. Allow to cool for 5 min., then add 2-5 ml of fresh B, mix, and after 30 min. measure the extinction at 530 $\text{m}\mu$. W. H. C. SHAW

220. Determination of free and total choline in serum and its application to the partition of serum phospholipids. L. Cohen (Chicago Univ. Clinic, Ill., U.S.A.). *J. Lab. Clin. Med.*, 1959, 53 (4), 629-637.—From a study of the microbiological method of Luecke and Pearson for the assay of total serum choline (*J. Biol. Chem.*, 1944, 153, 259) it is concluded that results given are valid but, contrary to the authors' findings, no free choline could be detected after the removal of interfering substances by chromatography on Decalco. Results on normal men showed that 68 to 90% of the serum phospholipids contain choline (sphingomyelin and lecithin), the remainder (kephalins) do not.

W. H. C. SHAW

221. Fluorescence reaction for the determination of 5-hydroxytryptamine by paper chromatography. P. F. Crosti (Univ. Milan, Italy). *Giorn. Biochim.*, 1958, 7, 97-101.—5-Hydroxytryptamine (I), 5-hydroxy-NN'-dimethyltryptamine and (to a less degree) 5-hydroxyindol-3-ylacetic acid on chromatograms prepared with *n*-butanol-acetic acid-water or *n*-butanol satd. with N HCl as solvents, showed an intense golden-yellow fluorescence when sprayed with 3 N HCl and exposed to u.v. light. Indole, indol-3-ylacetic acid, tryptophan, 4(or 5)-methyltryptophan, tryptamine, indolylmethylmethylamine and tyrosine did not give this fluorescence. The best acid for the determination was 3 N HCl and the limit of detection was 0.02 μ g of I. After evaporation of the acid the fluorescence could be re-developed by a new spray and, after elution of the spots and further chromatography, the presence of I was confirmed by HCl spraying.

CHEM. ABSTR.

222. Mildly alkaline (pH 8) solvent for the isolation, by paper chromatography, of purines, pyrimidines and their nucleosides and nucleotides. G. Hems (Middlesex Hosp., London, England). *Arch. Biochem. Biophys.*, 1959, 82 (2), 485-487.—Ascending chromatography is carried out on Whatman No. 1 paper at room temp. for 8 hr. with 85% saturated aq. ammonium bicarbonate soln. Thirty R_F values are listed.

W. H. C. SHAW

223. Ultra-violet absorption spectra of DPN [diphosphopyridine nucleotide] and analogues of DPN. J. M. Siegel, G. A. Montgomery and R. M. Bock (Pabst Lab., Milwaukee, Wis., U.S.A.). *Arch. Biochem. Biophys.*, 1959, 82 (2), 288-299.—The absorption spectra of specially purified DPN in oxidised and reduced forms, and of the cyanide addition compound, are presented together with comparable spectra of 3-acetylpyridine-, 3-pyridine-aldehyde-, deamino-, 3-acetylpyridinedeamino- and 3-pyridinealdehydedeamino-DPN. The increased extinctions observed after enzymatic hydrolysis are discussed.

W. H. C. SHAW

224. Separation of amino acids on ion-exchange resins by elution with water and aqueous ethanol. J. F. Thompson and C. J. Morris (Agric. Res. Service, U.S. Dept. Agric., Ithaca, N.Y.). *Arch. Biochem. Biophys.*, 1959, 82 (2), 380-386.—The elution patterns of amino acids from a sulphonic acid resin (Dowex 50-X4) (Na^+ form), a quaternary ammonium resin (Dowex 1-X2) (Cl^- form) and a carboxylic resin (Amberlite IRC-50) (H^+ form) are given. Good separations of acidic, basic and non- α -amino acids were attained by elution with water or 25% ethanol at room temp. and pH 6 to 8 on

the three resins. The partial resolution of neutral α -amino acids, β -alanine and γ -aminobutyric acid was achieved on Dowex 1-X2. W. H. C. SHAW

225. Anomalous reactions with the amino-nitrogen determination. Reaction of the $-\text{NH}-\text{CO}-$ group with nitrous acid. G. Kainz and H. Huber (II Chem. Inst., Univ., Vienna, Austria). *Mikrochim. Acta*, 1959, (4), 563-571 (in German).—The anomalous evolution of gas obtained when compounds containing the $-\text{NH}-\text{CO}-$ group react with HNO_2 was investigated. The reaction was conducted at various temp. with six compounds, and the gaseous products (N , N_2O and CO_2) were measured. A probable explanation for the anomaly is discussed.

G. P. COOK

226. Quantitative determination of free lysine in urine by two-dimensional paper chromatography. L. F. Kerley (Melbourne Univ., Australia). *J. Lab. Clin. Med.*, 1959, 53 (1), 149-155.—By the method proposed, satisfactory separation of lysine from ornithine and arginine is achieved. Two-dimensional chromatography of the sample at pH 2 is carried out on Whatman No. 1 paper by the ascending technique with 80% aq. phenol in the first dimension. After drying the paper, the second development is with a 65% soln. of a mixture of 2:4- and 2:5-lutidine. The paper is then treated with ninhydrin reagent and the amount of lysine is determined by a scanning device and compared with standards run on the same paper.

W. H. C. SHAW

227. Simplified process for determining tryptophan. Tryptophan peptide value. C. H. Brieskorn and H.-W. Berg (Inst. f. Pharm. u. Lebensmittelchem., Univ., Münster i. Westf., Germany). *Z. Lebensmittelforsch.*, 1959, 109 (4), 302-306.—Winkler's modification of the colour reaction of Adamkiewicz and Hopkins with glyoxylic acid and CuSO_4 for determining the tryptophan content of proteins was used after the removal of any accompanying fat, phosphatide or carbohydrate. If the protein is not completely hydrolysed, but only dissolved, the "tryptophan peptide value" is obtained. When this is multiplied by the factor 0.64 the result (for animal proteins) is in good agreement with the tryptophan value of albumin. This method is useful in confirming the biological value of a protein-containing food.

S.C.I. ABSTR.

228. Polarographic determination of histidine in the presence of leucine and methionine. Z. Paspová (Forschungsinst. Lebensmitteltech., Prague). *Nahrung*, 1958, 2, 135-139.—Polarographic curves are presented for the determination of histidine (I) in gelatin hydrolysates based on the reduction of Ni^{3+} in buffer soln. (0.1 M aq. $\text{NH}_3 \cdot \text{NH}_4\text{Cl}$) at pH 9.5. By this method I can be determined in the presence of leucine and methionine.

CHEM. ABSTR.

229. Simple method for the quantitative determination of small amounts of protein with an indicator. P. G. Scheuren (Med. Univ. Clinic, Tübingen). *Klin. Wochschr.*, 1959, 37 (6), 304-305.—The protein soln. (urine or diluted serum) is added to a soln. of bromophenol blue, buffered at pH 3.0, and the colour change produced, due to the so-called "protein error," is measured photometrically at 618 m μ . Beer's law is obeyed for protein concn. of 3 to 40 mg per 100 ml. Previous dialysis of the protein soln. against 0.9% NaCl soln. will remove a "salt error," which in most cases is

negligible. Only small amounts of soln. are required for this procedure, which is simple, accurate and sensitive. D. B. PALMER

230. Effects of ionic strength on the relative mobility of abnormal serum proteins. N. Ressler, N. A. Nelson, W. P. Richards and T. May (Wayne County Gen. Hosp., Eloise, Mich., U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (2), 178-185.—The mobilities of abnormal serum proteins during electrophoresis are found to vary with the buffer concn. and the reasons for this dependence are discussed. A simple method is described to determine what buffer concn. is suitable for any given macroglobulin. W. H. C. SHAW

231. Determination of mercapto groups in ovalbumin with ferricyanide. J. M. Katyal and G. Gorin (Oklahoma State Univ., Stillwater, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **82** (2), 319-329.—A method for the titration of mercapto groups in denatured ovalbumin is based on oxidation with 0.002 M $K_2Fe(CN)_6$ in the presence of M phosphate buffer, pH 7.1. The titration is followed with polarised electrodes, and the vol. of titrant required for the sample is determined graphically from the rectilinear increase in current after the end-point has been passed. The result (4.0 groups per mol. of mol. wt. 45,000) for ovalbumin is confirmed spectroscopically. The effects of dodecyltrimethylammonium chloride or of sodium dodecyl sulphate as denaturants are studied. W. H. C. SHAW

232. New precipitation method for estimating serum β -lipoproteins. E. Boyle and R. V. Moore (South Carolina Med. Coll., Charleston, U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (2), 272-281.—The rapid and simple method described is based on the formation of a stable turbidity on the addition of serum (0.2 ml) to 3 ml of a soln. of K-agar (carrageenin extract) in phosphate buffer. The change in extinction at 540 $m\mu$ due to the turbidity correlates well with total cholesterol, total β -cholesterol and β_2 -cholesterol values. Ingested lipids do not interfere. W. H. C. SHAW

233. Determination of β -hydroxysterols in serum and tissues by the anthrone reaction. W. W. Webster, C. W. Nichols and I. L. Chaikoff (California Univ., Berkeley, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **82** (1), 195-202.—Lipids and sterols are extracted from plasma (0.5 ml) and tissues by the procedures described, and the concentrated acetone-ethanol extracts, after saponification and neutralisation, are treated with digitonin. The mixture is set aside overnight and the pptd. sterol digitonides are separated by centrifugation. A single re-pptn. from 50% methanol serves to remove any occluded digitonin. The purified digitonides are dissolved in glacial acetic acid and one aliquot is taken for the determination of cholesterol. A further aliquot is treated with anthrone in 60% aq. H_2SO_4 and the mixture is heated at 100° for 10 min., then cooled in an ice-bath. The extinction is read at 625 $m\mu$ and the total β -hydroxysterols determined by reference to a standard curve prepared with digitonin. The amount attributable to cholesterol is then deducted. W. H. C. SHAW

234. Purification of paper extracts in the quantitative determination of steroids. G. W. Oertel and K. B. Eik-Nes (Dept. of Biol. Chem., Univ. of Utah, Salt Lake City, U.S.A.). *Naturwissenschaften*, 1959, **46** (8), 261-262.—The extracts from the

sample chromatogram and from a similar area of blank paper are evaporated to dryness *in vacuo* under N. The residues are dissolved in 15 ml of ethyl acetate and extracted successively with 10 ml of 0.5% H_2SO_4 (containing 10 mg of quinal), 10 ml of H_2O and 5 ml of H_2O . Both ethyl acetate soln. are then evaporated as before. The residues are then suitable for the colorimetric determination of steroids. The method is suitable, for example, for the determination of oestrone, oestradiol and oestriol in plasma, in concn. $>0.1 \mu g$ per 25 ml. S. BAAR

235. Separation of some steroids by glass-(fibre) paper chromatography. J. G. Hamilton and J. W. Dieckert (Tulane Univ., New Orleans, La., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **82** (1), 212-219.—Chromatography of corticosteroids and oestrogens is carried out on glass-fibre paper treated with 0.1 M KH_2PO_4 dil. potassium silicate, silicic acid or alumina, developed with isooctane, isooctane-benzene (1:2), benzene, or benzene-ethanol (200:1). The compounds are located by spraying with conc. H_2SO_4 and heating. R_F values for 15 steroids on the paper treated with potassium silicate are given. The separation of steroid alcohols from the corresponding ketones and of two pairs of *cis-trans* isomers was achieved. W. H. C. SHAW

236. Separation of some bile acids by glass-(fibre) paper chromatography. J. G. Hamilton and J. W. Dieckert (Tulane Univ., New Orleans, La., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **82** (1), 203-211.—Chromatography is carried out on glass-fibre paper impregnated with 0.1 M KH_2PO_4 dil. potassium silicate or silicic acid, developed with benzene-ethanol mixtures or with $CHCl_3$. R_F values for 11 bile acids and their ketonic oxidation products are listed. The separation of some *cis-trans* isomers of hyocholic acid was achieved, but not that of certain positional isomers of bile acids. W. H. C. SHAW

237. Differential determination of bile acids in bile by paper chromatography. I. Separation of free and conjugated bile acids by paper chromatography. Nobuyuki Watanabe (Dept. of Surgery, Fac. of Med., Kyushu Univ., Fukuoka, Japan). *Kyushu J. Med. Sci.*, 1959, **10** (1), 17-25.—Paper partition chromatographic procedures have been devised for the separation and determination of free, glycine-conjugated and taurine-conjugated bile acids. Free and glycine-conjugated acids can be separated by an ascending technique with toluene-glacial acetic acid-water (5:5:1) as the mobile phase at 15° to 25° on paper equilibrated with the vapour of 70% acetic acid. Taurine-conjugated bile acids may also be separated with ethyl butyrate-heptane (9:1) as the mobile phase at 25° to 30°. The spots on the chromatograms are revealed by spraying the paper with a 30% ethanolic soln. of molybdophosphoric acid and heating at 100° to 120°. Ultra-violet absorption techniques are used for the determination of individual acids. Interfering lipids may be removed by (i) preliminary chromatography with 50% aq. methanol (pH 12) as the solvent; lipids remain at the starting point and can be cut off, and chromatography with the appropriate solvent is then continued on the same paper; or (ii) extraction with light petroleum (boiling-range 40° to 60°) from a soln. of the crude bile acids in 50% aq. ethanol. The latter method is preferable since the complete removal of lipids by (i) is not possible. Some results are discussed.

220. Determination of free and total choline in serum and its application to the partition of serum phospholipids. L. Cohen (Chicago Univ. Clinic, Ill., U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (4), 629-637.—From a study of the microbiological method of Luecke and Pearson for the assay of total serum choline (*J. Biol. Chem.*, 1944, **153**, 259) it is concluded that results given are valid but, contrary to the authors' findings, no free choline could be detected after the removal of interfering substances by chromatography on Decalco. Results on normal men showed that 68 to 90% of the serum phospholipids contain choline (sphingomyelin and lecithin), the remainder (kephalins) do not.

W. H. C. SHAW

221. Fluorescence reaction for the determination of 5-hydroxytryptamine by paper chromatography. P. F. Crosti (Univ. Milan, Italy). *Giorn. Biochim.*, 1958, **7**, 97-101.—5-Hydroxytryptamine (I), 5-hydroxy-NN'-dimethyltryptamine and (to a less degree) 5-hydroxyindol-3-ylacetic acid on chromatograms prepared with *n*-butanol-acetic acid-water or *n*-butanol satd. with *N* HCl as solvents, showed an intense golden-yellow fluorescence when sprayed with 3 *N* HCl and exposed to u.v. light. Indole, indol-3-ylacetic acid, tryptophan, 4(or 5)-methyltryptophan, tryptamine, indolylmethyl-dimethylamine and tyrosine did not give this fluorescence. The best acid for the determination was 3 *N* HCl and the limit of detection was 0.02 μ g of I. After evaporation of the acid the fluorescence could be re-developed by a new spray and, after elution of the spots and further chromatography, the presence of I was confirmed by HCl spraying.

CHEM. ABSTR.

222. Mildly alkaline (pH 8) solvent for the isolation, by paper chromatography, of purines, pyrimidines and their nucleosides and nucleotides. G. Hems (Middlesex Hosp., London, England). *Arch. Biochem. Biophys.*, 1959, **82** (2), 485-487.—Ascending chromatography is carried out on Whatman No. 1 paper at room temp. for 8 hr. with 85% saturated aq. ammonium bicarbonate soln. Thirty R_F values are listed.

W. H. C. SHAW

223. Ultra-violet absorption spectra of DPN [diphosphopyridine nucleotide] and analogues of DPN. J. M. Siegel, G. A. Montgomery and R. M. Bock (Pabst Lab., Milwaukee, Wis., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **82** (2), 288-299.—The absorption spectra of specially purified DPN in oxidised and reduced forms, and of the cyanide addition compound, are presented together with comparable spectra of 3-acetylpyridine-, 3-pyridine-aldehyde-, deamino-, 3-acetylpyridinedeamino- and 3-pyridinealdehydedeamino-DPN. The increased extinctions observed after enzymatic hydrolysis are discussed.

W. H. C. SHAW

224. Separation of amino acids on ion-exchange resins by elution with water and aqueous ethanol. J. F. Thompson and C. J. Morris (Agric. Res. Service, U.S. Dept. Agric., Ithaca, N.Y.). *Arch. Biochem. Biophys.*, 1959, **82** (2), 380-386.—The elution patterns of amino acids from a sulphonic acid resin (Dowex 50-X4) (Na^+ form), a quaternary ammonium resin (Dowex 1-X2) (Cl^- form) and a carboxylic resin (Amberlite IRC-50) (H^+ form) are given. Good separations of acidic, basic and non- α -amino acids were attained by elution with water or 25% ethanol at room temp. and pH 6 to 8 on

the three resins. The partial resolution of neutral α -amino acids, β -alanine and γ -aminobutyric acid was achieved on Dowex 1-X2. W. H. C. SHAW

225. Anomalous reactions with the amino-nitrogen determination. Reaction of the $-\text{NH}-\text{CO}-$ group with nitrous acid. G. Kainz and H. Huber (II Chem. Inst., Univ., Vienna, Austria). *Mikrochim. Acta*, 1959, (4), 563-571 (in German).—The anomalous evolution of gas obtained when compounds containing the $-\text{NH}-\text{CO}-$ group react with HNO_2 was investigated. The reaction was conducted at various temp. with six compounds, and the gaseous products (N , N_2O and CO_2) were measured. A probable explanation for the anomaly is discussed.

G. P. COOK

226. Quantitative determination of free lysine in urine by two-dimensional paper chromatography. L. F. Kerley (Melbourne Univ., Australia). *J. Lab. Clin. Med.*, 1959, **53** (1), 149-155.—By the method proposed, satisfactory separation of lysine from ornithine and arginine is achieved. Two-dimensional chromatography of the sample at pH 2 is carried out on Whatman No. 1 paper by the ascending technique with 80% aq. phenol in the first dimension. After drying the paper, the second development is with a 65% soln. of a mixture of 2:4- and 2:5-lutidine. The paper is then treated with ninhydrin reagent and the amount of lysine is determined by a scanning device and compared with standards run on the same paper.

W. H. C. SHAW

227. Simplified process for determining tryptophan. Tryptophan peptide value. C. H. Brieskorn and H.-W. Berg (Inst. f. Pharm. u. Lebensmittelchem., Univ., Münster i. Westf., Germany). *Z. Lebensmitteluntersuch.*, 1959, **109** (4), 302-306.—Winkler's modification of the colour reaction of Adamkiewicz and Hopkins with glyoxylic acid and CuSO_4 for determining the tryptophan content of proteins was used after the removal of any accompanying fat, phosphatide or carbohydrate. If the protein is not completely hydrolysed, but only dissolved, the "tryptophan peptide value" is obtained. When this is multiplied by the factor 0.64 the result (for animal proteins) is in good agreement with the tryptophan value of albumin. This method is useful in confirming the biological value of a protein-containing food.

S.C.I. ABSTR.

228. Polarographic determination of histidine in the presence of leucine and methionine. Z. Paspová (Forschungsinstit. Lebensmitteltech., Prague). *Nahrung*, 1958, **2**, 135-139.—Polarographic curves are presented for the determination of histidine (I) in gelatin hydrolysates based on the reduction of Ni^{2+} in buffer soln. (0.1 *M* aq. $\text{NH}_3 \cdot \text{NH}_4\text{Cl}$) at pH 9.5. By this method I can be determined in the presence of leucine and methionine.

CHEM. ABSTR.

229. Simple method for the quantitative determination of small amounts of protein with an indicator. P. G. Scheurle (Med. Univ. Clinic, Tübingen). *Klin. Wochschr.*, 1959, **37** (6), 304-305.—The protein soln. (urine or diluted serum) is added to a soln. of bromophenol blue, buffered at pH 3.0, and the colour change produced, due to the so-called "protein error," is measured photometrically at 618 $\text{m}\mu$. Beer's law is obeyed for protein concn. of 3 to 40 mg per 100 ml. Previous dialysis of the protein soln. against 0.9% NaCl soln. will remove a "salt error," which in most cases is

negligible. Only small amounts of soln. are required for this procedure, which is simple, accurate and sensitive.

D. B. PALMER

230. Effects of ionic strength on the relative mobility of abnormal serum proteins. N. Ressler, N. A. Nelson, W. P. Richards and T. May (Wayne County Gen. Hosp., Eloise, Mich., U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (2), 178-185.—The mobilities of abnormal serum proteins during electrophoresis are found to vary with the buffer concn. and the reasons for this dependence are discussed. A simple method is described to determine what buffer concn. is suitable for any given macroglobulin.

W. H. C. SHAW

231. Determination of mercapto groups in ovalbumin with ferricyanide. J. M. Katyal and G. Gorin (Oklahoma State Univ., Stillwater, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **82** (2), 319-329.—A method for the titration of mercapto groups in denatured ovalbumin is based on oxidation with 0.002 M $K_3Fe(CN)_6$ in the presence of M phosphate buffer, pH 7.1. The titration is followed with polarised electrodes, and the vol. of titrant required for the sample is determined graphically from the rectilinear increase in current after the end-point has been passed. The result (4.0 groups per mol. of mol. wt. 45,000) for ovalbumin is confirmed spectroscopically. The effects of dodecyltrimethylammonium chloride or of sodium dodecyl sulphate as denaturants are studied.

W. H. C. SHAW

232. New precipitation method for estimating serum β -lipoproteins. E. Boyle and R. V. Moore (South Carolina Med. Coll., Charleston, U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (2), 272-281.—The rapid and simple method described is based on the formation of a stable turbidity on the addition of serum (0.2 ml) to 3 ml of a soln. of K-agar (carrageenin extract) in phosphate buffer. The change in extinction at 540 m μ due to the turbidity correlates well with total cholesterol, total β -cholesterol and β_2 -cholesterol values. Ingested lipids do not interfere.

W. H. C. SHAW

233. Determination of β -hydroxysterols in serum and tissues by the anthrone reaction. W. W. Webster, C. W. Nichols and I. L. Chaikoff (California Univ., Berkeley, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **82** (1), 195-202.—Lipids and sterols are extracted from plasma (0.5 ml) and tissues by the procedures described, and the concentrated acetone-ethanol extracts, after saponification and neutralisation, are treated with digitonin. The mixture is set aside overnight and the pptd. sterol digitonides are separated by centrifugation. A single re-pptn. from 50% methanol serves to remove any occluded digitonin. The purified digitonides are dissolved in glacial acetic acid and one aliquot is taken for the determination of cholesterol. A further aliquot is treated with anthrone in 60% aq. H_2SO_4 and the mixture is heated at 100° for 10 min., then cooled in an ice-bath. The extinction is read at 625 m μ and the total β -hydroxysterols determined by reference to a standard curve prepared with digitonin. The amount attributable to cholesterol is then deducted.

W. H. C. SHAW

234. Purification of paper extracts in the quantitative determination of steroids. G. W. Oertel and K. B. Eik-Nes (Dept. of Biol. Chem., Univ. of Utah, Salt Lake City, U.S.A.). *Naturwissenschaften*, 1959, **46** (8), 261-262.—The extracts from the

sample chromatogram and from a similar area of blank paper are evaporated to dryness *in vacuo* under N. The residues are dissolved in 15 ml of ethyl acetate and extracted successively with 10 ml of 0.5% H_2SO_4 (containing 10 mg of quinal), 10 ml of H_2O and 5 ml of H_2O . Both ethyl acetate soln. are then evaporated as before. The residues are then suitable for the colorimetric determination of steroids. The method is suitable, for example, for the determination of oestrone, oestradiol and oestriol in plasma, in concn. >0.1 μ g per 25 ml.

S. BAAR

235. Separation of some steroids by glass-(fibre) paper chromatography. J. G. Hamilton and J. W. Dieckert (Tulane Univ., New Orleans, La., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **82** (1), 212-219.—Chromatography of corticosteroids and oestrogens is carried out on glass-fibre paper treated with 0.1 M KH_2PO_4 dil. potassium silicate, silicic acid or alumina, developed with isooctane, isooctane-benzene (1:2), benzene, or benzene-ethanol (200:1). The compounds are located by spraying with conc. H_2SO_4 and heating. R_F values for 15 steroids on the paper treated with potassium silicate are given. The separation of steroid alcohols from the corresponding ketones and of two pairs of *cis-trans* isomers was achieved.

W. H. C. SHAW

236. Separation of some bile acids by glass-(fibre) paper chromatography. J. G. Hamilton and J. W. Dieckert (Tulane Univ., New Orleans, La., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **82** (1), 203-211.—Chromatography is carried out on glass-fibre paper impregnated with 0.1 M KH_2PO_4 dil. potassium silicate or silicic acid, developed with benzene-ethanol mixtures or with $CHCl_3$. R_F values for 11 bile acids and their ketonic oxidation products are listed. The separation of some *cis-trans* isomers of hyocholic acid was achieved, but not that of certain positional isomers of bile acids.

W. H. C. SHAW

237. Differential determination of bile acids in bile by paper chromatography. I. Separation of free and conjugated bile acids by paper chromatography. Nobuyuki Watanabe (Dept. of Surgery, Fac. of Med., Kyushu Univ., Fukuoka, Japan). *Kyushu J. Med. Sci.*, 1959, **10** (1), 17-25.—Paper partition chromatographic procedures have been devised for the separation and determination of free, glycine-conjugated and taurine-conjugated bile acids. Free and glycine-conjugated acids can be separated by an ascending technique with toluene-glacial acetic acid-water (5:5:1) as the mobile phase at 15° to 25° on paper equilibrated with the vapour of 70% acetic acid. Taurine-conjugated bile acids may also be separated with ethyl butyrate-heptane (9:1) as the mobile phase at 25° to 30°. The spots on the chromatograms are revealed by spraying the paper with a 30% ethanolic soln. of molybdophosphoric acid and heating at 100° to 120°. Ultra-violet absorption techniques are used for the determination of individual acids. Interfering lipids may be removed by (i) preliminary chromatography with 50% aq. methanol (pH 12) as the solvent; lipids remain at the starting point and can be cut off, and chromatography with the appropriate solvent is then continued on the same paper; or (ii) extraction with light petroleum (boiling-range 40° to 60°) from a soln. of the crude bile acids in 50% aq. ethanol. The latter method is preferable since the complete removal of lipids by (i) is not possible. Some results are discussed.

II. Quantitative micro-determination of bile acids by ultra-violet absorption. Nobuyuki Watanabe. *Ibid.*, 1959, 10 (1), 26-36.—The quant. determination of bile acids (previously separated by paper partition chromatography) by measurement of the u.v. absorption in 65% H_2SO_4 is described. Experiments designed to establish the optimum conditions are detailed, and it was found that heating the separated bile acids at 28° for 60 min. before measuring the extinction is preferable since, under these conditions, the extinction has only a small standard deviation and is not significantly affected by Fe^{2+} or "dirt" on the filter-paper. The possibility of determining conjugated chenodeoxycholic acid and conjugated deoxycholic acid in soln. containing both is indicated. The results obtained in the determination of bile acids in human bile and for the recovery of pure bile acids added to human bile are discussed. The separation of tauro-conjugated bile acids from Japanese human bile is reported for the first time. S. M. MARSH

238. Determination of progesterone in human blood plasma. G. W. Oertel, S. P. Weiss and K. B. Eik-Nes (Dept. of Biochem., Univ. of Utah Coll. of Med., Salt Lake City, U.S.A.). *J. Clin. Endocrin. & Metabolism*, 1959, 19 (2), 213-218.—Plasma (10 to 20 ml) is extracted with ethanol (3 x 30 to 60 ml) by mechanical shaking for 15 min. and centrifuging. The combined extract is evaporated to dryness at 40°. Lipid material is removed by dissolving the residue in 70% methanol (10 ml), holding at -15° for 15 hr. and centrifuging for 15 min. at 2000 r.p.m. in a refrigerated centrifuge. The supernatant liquid is removed and the ppt. washed with ice-cold 70% methanol (2 ml). Water (15 ml) is added and the progesterone (I) is extracted with hexane (3 x 15 ml); the combined hexane extract is evaporated *in vacuo*. The residue is transferred to a paper strip with methanol- $CHCl_3$ (1:1) (3 x 0.2 ml) and chromatographed with methanol-benzene (1:9) for 3 to 4 hr. to concentrate the steroids. The steroid-containing portion of this strip is then cut off and transferred to another strip impregnated with propane-1:2-diol-methanol (1:1) and chromatographed with methylcyclohexane. In the chromatography, deoxycorticosterone and I (50 µg) are used as reference compounds for locating the sample spots. The area of the sample strip containing the I is cut out and extracted with methanol (3 x 2 ml), two pieces of a blank strip are treated similarly and 10 µg of I is added to one. The extracts are evaporated to dryness *in vacuo*, the residues are dissolved in benzene (10 ml) and extracted with 0.1 N H_2SO_4 (10 ml) and H_2O (2 x 10 ml), and the benzene is removed *in vacuo*. The dry residues are dissolved in 1-2 ml of 80% ethanol-conc. H_2SO_4 (1:2, by vol.), warmed at 60° for 15 min., then cooled, and the absorption is measured at 260, 290 and 320 mµ. The corrected absorption at 290 mµ is obtained by subtracting one-half of the sum of the other two readings. The amount of I is finally calculated by the determination of the recovery of labelled and unlabelled I (86 to 101%).

H. F. W. KIRKPATRICK

239. Determination of pepsinogen (uropepsin) in urine. G. D. Simbirtseva (Pediatric and San-Hygiene Faculty, L'vov Med. Inst., U.S.S.R.). *Lab. Delo*, 1959, 5 (2), 53-56.—The method is based on the coagulation of milk casein by activated urinary pepsinogen. Procedure for the activation of urinary pepsinogen—To urine (2 ml) at pH > 3

add 2 N HCl (0.1 ml) and 2% methyl orange soln. (1 drop) and place in a water bath at 37° for 1 hr. Procedure for the determination of urinary pepsinogen—All reagents should be at 37°. Make an aliquot (e.g., 0.1 ml) of the activated urine up to 1 ml with H_2O , add acetate buffer (0.1 ml) at pH 4.9 and shake well; add a milk-acetate mixture (0.5 ml) and simultaneously start the timer. Shake the mixture well and place in a water bath at 37°, shaking gently every 10 to 15 sec. The first appearance of a coagulum must be noted with an accuracy of ±5 sec. Calculate the pepsinogen from the formula—units per hr. = $[V/(10vh)](100/t)1.32$, where V is the total vol. (ml) of urine, v is vol. (ml) of urine in the tube, t is time (sec.) to the appearance of a coagulum, and h is time (hr.) from the collection of the urine. Results showed that, with healthy individuals, urinary pepsinogen fluctuates between 12 and 35 units per hr. The results for diseased individuals are tabulated. K. R. C.

240. Turbidimetric determination of deoxyribonuclease activity. J. C. Houck (Georgetown Univ. Hosp., Washington, D.C., U.S.A.). *Arch. Biochem. Biophys.*, 1959, 82 (1), 135-144.—The method described is based on the formation of a turbid colloid, stabilised with gelatin, by polymerised ribonucleic acid and acidified serum albumin. To 0.5 ml of purified deoxyribonucleic acid soln. (0.8 to 1.2 mg per ml) in 0.1 M acetate buffer (pH 6.3) (containing 0.1 M $MgCl_2$) is added 0.5 ml of an aq. soln. of the deoxyribonuclease sample. After incubation for 30 min. at 26°, 5 ml of serum albumin (0.3 mg per ml) and of gelatin (1 mg per ml) in 0.1 M acetate buffer (pH 3.7) is added and the mixture is heated at 37° for <5 min. The turbidity is then measured at 450 mµ. The method is suitable for pancreatic and serum deoxyribonucleases, on which the influence of pH, temp. and bivalent cation activation is studied. W. H. C. SHAW

241. Ribonuclease assay based on uridine phosphate determination. S. R. Dickman and K. Trupin (Utah Univ. Coll. Med., Salt Lake City, U.S.A.). *Arch. Biochem. Biophys.*, 1959, 82 (2), 355-361.—In the method described, the ribonuclease sample is incubated with ribonucleic acid (I) in buffer soln. at pH 5 for 10 min. at 37°. Unchanged I and nucleotides containing amino groups are pptd. at pH 4 with a uranyl acetate reagent containing $HClO_4$. After centrifugation the uridine cyclic phosphate remaining in the supernatant liquid is determined spectroscopically at 260 mµ. The influence of pH, time, ionic strength and concn. of the reactants is studied. W. H. C. SHAW

242. Estimation of anserinase activity by a low-temperature ninhydrin reaction. N. R. Jones (Torry Res. Station, Dept. of Sci. and Ind. Res., Aberdeen, Scotland). *Biochem. J.*, 1959, 72 (3), 407-409.—Anserine reacts extremely slowly, almost negligibly, with ninhydrin reagent at 35°, whereas 1-methylhistidine and β-alanine, the two amino acids formed by the hydrolysis of anserine, react readily. This is the basis for a very sensitive, improved colorimetric method for the determination of low concn. of the enzyme, anserinase. The colour is measured at 570 mµ in a photo-electric absorptiometer. J. N. ASHLEY

See also Abstracts—26, Determination of K in blood serum. 42, Determination of Sr in bone. 84, Determination of NO_3^- in tissues. 149, Determination of Co in biological materials. 165, Analyses of cholanes and pregnanes.

Pharmaceutical analysis

243. Infra-red spectrophotometry as a testing procedure of U.S.P. XVI. A. R. Gennaro and A. Osol. *Amer. J. Pharm.*, 1958, **130** (11), 368-382.—The basic principles of i.r. spectrophotometry and the design and operation of a typical instrument are described. Examples are given of the application of the method to the testing of drugs. The spectra of cortisone, cortisol, prednisolone and prednisone are illustrated. N. E.

244. Systematic analysis of alkaloids with the aid of paper chromatography. D. Waldi (Kontroll-Lab., E. Merck A.-G., Darmstadt). *Arch. Pharm., Berlin*, 1959, **292** (4), 206-220.—The sample containing the unknown alkaloid was subjected to chromatography on formamide-impregnated paper, with solvent mixtures of differing polarity prepared from CHCl_3 , cyclohexane, diethylamine and light petroleum in various proportions. Alkaloids were divided into four groups according to their migration with the various solvents. Individual members of the groups were identified by the determination of their R_F factor (i.e., $R_F \times$ "fixed" R_F of a standard member of that group/observed R_F of the standard member), by their fluorescence under u.v. light and by their reaction with various reagents ($\text{KI}-\text{H}_2\text{PtCl}_6$, ninhydrin, p -dimethylaminobenzaldehyde, diazotised sulphanilic acid and chloramine T-trichloroacetic acid). Results are tabulated for 70 alkaloids. A. G. COOPER

245. Determination of ergot alkaloids with p -dimethylaminobenzaldehyde. R. Voigt (Pharm. Inst., Humboldt Univ., Berlin). *Mikrochim. Acta*, 1959, (4), 619-629 (in German).—The various forms of the p -dimethylaminobenzaldehyde reagent for the determination of ergot alkaloids do not always give a quant. colour reaction. The effects of the concn. of alkaloid, acid and oxidant (FeCl_3) and the influence of light, particularly u.v., were studied, and the use of a reagent prepared specifically for ergot-alkaloid determinations is recommended. G. P. COOK

246. Analysis of sympathomimetics. IV. The determination of ephedrine in pharmaceutical preparations by titration in a non-aqueous medium. R. Pohloudek-Fabini and K. König (Pharm.-Chem. Inst. der Ernst-Moritz-Arndt Univ., Greifswald, Germany). *Pharm. Zentrbl.*, 1959, **98** (4), 176-181.—To determine ephedrine hydrochloride (I) alone or in the presence of phenacetin or phenobarbitone, prepare a soln. of the sample (containing ≈ 50 mg of I) in glacial acetic acid, titrate with 0.05 N HClO_4 in dioxan, with crystal violet as indicator, to a blue end-point, add mercuric acetate and complete the titration. Calculate the content of I from the second titre. To determine I in the presence of leptazol (II), extract the sample with diethyl ether (and evaporate and weigh the extracted II if desired); then titrate the ether-insoluble residue in glacial acetic acid with HClO_4 as described above. The recovery of I is ≈ 99 to 101%. A. R. ROGERS

247. Estimation of vasicine in *Adhatoda vasica* Nees. L. V. Kannan, S. K. Srivastava and G. K. Ray (Central Drug Res. Inst., Lucknow). *Indian J. Pharm.*, 1959, **21** (4), 108-110.—Extract the powdered drug (20 g) in a Soxhlet apparatus with 95% ethanol. Evaporate the extract almost to dryness, add 5% Pb acetate soln. (20 ml), filter, add dil. H_2SO_4 (25 ml) and filter again. Extract

the filtrate with CHCl_3 (3×10 ml) and wash the combined CHCl_3 soln. with 0.1 N H_2SO_4 (10 ml). Mix the aq. phases, make alkaline with aq. NH_3 and extract with CHCl_3 until there is no further reaction with Mayer's reagent. Evaporate the CHCl_3 extracts, dissolve the residue in 0.1 N HCl (20 ml) and titrate with 0.1 N NaOH , with bromothymol blue as indicator. A. R. ROGERS

248. Quantitative determination of aloin in *Aloe capensis*. II. Colorimetric determination. L. Kraus (Państwowe Inst. Kontroli Lekow w Pradze). *Acta Polon. Pharm.*, 1959, **16** (3), 223-224.—Descending chromatography is used on Whatman paper No. 1, with n -butanol-water-glacial acetic acid (4:5:1) as the mobile phase. The developed and dried chromatogram is examined in u.v. light, the aloin spots (intense yellow) are cut out and eluted with acetone, and the soln. is oxidised with FeCl_3 . The colour is then measured in a Pulfrich photometer, with a 5-cm cell and filter S53. W. B. MIAKOWSKI

249. New colorimetric method for determining rhaponticin in underground parts of rhubarb after chromatographic separation. M. Henneberg and P. Horak (Państwowy Inst. Nauk. Lezcz. Surowców Roślin. w Poznani). *Acta Polon. Pharm.*, 1959, **16** (3), 189-196.—This analysis of rhubarb rhizome is based on the determination of the amount of rhaponticin (I), as an index of the degree of adulteration, by means of the reducing properties of the phenol groups of I, $\text{K}_3\text{Fe}(\text{CN})_6$, being reduced to $\text{K}_4\text{Fe}(\text{CN})_6$. For the analysis, 200 μ l of a 2% ethanolic extract of the sample, prepared at high temp., is applied to Whatman No. 1 paper and chromatographed by the descending technique with CHCl_3 -methanol-acetic acid (3:2:0.5), satd. with water. The developed chromatogram shows a characteristic colour in u.v. light. The spot is cut out and eluted with NaOH soln., and the soln. is treated first with 0.2% $\text{K}_3\text{Fe}(\text{CN})_6$ soln. and then with acid 0.06% $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$ soln. The extinction of the greenish-blue soln. is measured in a Pulfrich photometer with 1-cm cells and S72 filter, and compared with a standard curve for rhaponticin determined by Auterhoff's method (cf. Neuhoff and Auterhoff, *Anal. Abstr.*, 1955, **2**, 1644). As little as 5 μ g of rhaponticin can be determined. W. B. MIAKOWSKI

250. New types of salting-out paper chromatograms of antibiotics. J. Uri (Hung. Acad. Sci., Debrecen). *Nature*, 1959, **183**, 1188-1189.—Pure antibiotics and materials containing antibiotics were chromatographed on paper by the ascending technique with water and aq. soln. of NH_4Cl of increasing concn. as irrigating solvents, the spots being located by bio-autography. The results show that antibiotics can be divided into six groups, which are characterised by their R_F values with these solvents. The study confirmed and extended the findings of other workers. G. P. COOK

251. *Candida albicans* plate assay of nystatin. S. R. Carlson and J. W. Snyder (Upjohn Co., Kalamazoo, Mich., U.S.A.). *Antibiot. & Chemother.*, 1959, **9** (3), 139-144.—Details are given of a cylinder plate method with *Candida albicans* UC 1077 as test organism on an agar medium containing 5% of malt extract and 20% of glucose. The method is suitable for the routine assay of nystatin

soln. in phosphate buffer of pH 6.0, at concn. of 19 to 47 units per ml, over which range parallel response-curves are obtained. No interference in the assay was encountered from penicillin, novobiocin, erythromycin, tetracycline or dihydrostreptomycin.

W. H. C. SHAW

252. Identification of barbiturates. A. S. Curry (Home Office Forensic Sci. Lab., Harrogate, Yorks., England). *Nature*, 1959, **183**, 1052.—Isolate the weakly acidic ether-soluble fraction following tungstic acid pptn. of the sample of blood. Heat the extract with conc. H_2SO_4 at 100° for 1 hr., dilute with H_2O , extract into diethyl ether and examine the u.v. absorption spectrum of a soln. of the product in 0.5 N aq. NH_3 . Phenobarbitone is completely destroyed by this treatment. Barbitone, amylbarbitone and butobarbitone give max. absorption at 240 $m\mu$, and pentobarbitone and cyclobarbitone at 268 $m\mu$; quinalbarbitone gives very weak absorptions at 240, 266 and 315 $m\mu$. This test should be used in conjunction with the paper-chromatographic test described previously (cf. *Acta Pharm. Tox., Kbh.*, 1957, **13**, 357).

A. R. ROGERS

253. Coulometric micro-determination of Bromural (bromvaletone) (α -bromisovalerylurea) and carbromal (α -bromodiethylacetylurea). K. Kalinowski (Dept. of Pharm. Chem., Med. Acad., Łódź, Poland). *Acta Polon. Pharm.*, 1959, **16** (3), 225-229.—This method, based on the use of electrolytically generated Ag^+ for determining Br^- , is superior to that in which the external addition of Ag^+ is employed, but the conditions must be controlled carefully so as to avoid any side-reactions taking place on the generating electrodes. An accuracy within $\pm 1\%$ can then be achieved for quantities from 0.5 to 2.0 mg. The system involving the use of a copper-silver electrode pair without an externally applied voltage proved the most satisfactory, since it enables the end-point to be detected whatever the colour of the soln.

W. B. MIAKOWSKI

254. Coulometric determination of cyclobarbitone and hexobarbitone. K. Kalinowski and H. Baran (Dept. of Pharm. Chem., Med. Acad., Łódź). *Acta Polon. Pharm.*, 1959, **16** (3), 231-233.—A method based on the addition of Cl at a double bond is described, and it is claimed that cyclobarbitone (1.2 to 3.2 mg) and hexobarbitone (1.2 to 2.7 mg) can be determined with an accuracy of $\pm 0.7\%$, the time required being 10 min. Chlorine was generated electrolytically and the "dead stop" method was used with a platinum electrode pair.

W. B. MIAKOWSKI

255. Titration of some amines in propionic acid and propionic anhydride using colour indicators. H. Ellert, T. Jasiński and I. Pawelczak (Dept. of Pharm. Chem., Med. Acad., Gdańsk). *Acta Polon. Pharm.*, 1959, **16** (3), 235-239.—The titration of phenazone (I), caffeine (II) or theophylline (III) in pure propionic acid proved impossible because the addition of 0.1 N $HClO_4$ to the soln. of I or II caused the formation of oily drops which absorb the indicator, and with III the colour change was not sharp. In a mixture of propionic acid and propionic anhydride (1:1), or in pure propionic anhydride, accurate results were obtained for I, II and III with methyl violet, malachite green (C.I. Basic Green 4), Nile blue (C.I. Basic Blue 12), neutral red, safranin (C.I. Basic Red 2) and Sudan

III (C.I. Solvent Red 23) as indicators. Correct results were also obtained for amidopyrine (IV) in propionic acid with methyl red, malachite green, neutral red, safranin and Tropaeolin OO (C.I. Acid Orange 5). In propionic anhydride, IV gives a perceptible colour change only in the presence of Sudan III, which appears when 1 mole of IV combines with 2 moles of $HClO_4$. The accuracy for I, II and IV was $\pm 5\%$ and for III 0.5 to 2%.

W. B. MIAKOWSKI

256. Stability and determination of Amphisol [amiphenazole] in aqueous solution. J. H. Sørensen (Nordisk Droge's Synteslab., Copenhagen). *Dansk Tidsskr. Farm.*, 1959, **33** (4), 61-75 (from English summary).—Amiphenazole (I) undergoes hydrolysis in aq. soln. between pH 3 and 6 to form 2-amino-4-hydroxy-5-phenylthiazole (II) and ammonium bromide. A spectrometric method for the determination of I and II is described. The extinction curves for I and II intersect at 225 $m\mu$, permitting calculation of the total quantity of I plus II. Between 253 $m\mu$ and 257 $m\mu$ the extinction curves are approx. parallel. There is a linear relationship between extinction and concn. in this region and, assuming that the extinctions of I and II are additive, the concn. of I and II may be calculated. The results are compared with those obtained by the reineckate method (Lundgren, cf. *Anal. Abstr.*, 1956, **3**, 2274).

A. G. COOPER

257. New method of estimation of tolbutamide. P. M. Parikh and S. P. Mukherji (Zandu Pharmaceutical Works Ltd., Bombay). *Indian J. Pharm.*, 1959, **21** (4), 110-111.—Shake the powdered sample of tablets (containing 0.8 g of tolbutamide) with warm acetone (10 ml) and dilute with 0.2 N NaOH to 50 ml. Shake for 2 min. and filter through paper. Neutralise a 20-ml aliquot of the filtrate to phenolphthalein with 3% acetic acid, add 0.1 N $AgNO_3$ (20 ml), shake for 3 min. and filter through sintered glass. Wash the ppt. with H_2O (3×5 ml). Acidify the combined filtrate and washings with HNO_3 (10 ml) and titrate with 0.05 N NH_4SCN , with $(NH_4)_2SO_4.Fe_2(SO_4)_3$ as indicator. Perform a blank determination. Tablet excipients and lubricants (lactose, starch, calcium phosphates, talc, magnesium stearate and gum acacia) cause little or no interference.

A. R. ROGERS

258. Determination by ultra-violet absorption spectra of 6-mercaptopurine and its hydrate. Takeji Noto, Hiroshi Sawada, Yoshishige Sato, Nakatomi Fukuda and Yoshiyuki Inoue (Tanabe Seiyaku Osaka Plant). *Ann. Rep. Gohei Tanabe Co. Ltd.*, 1958, **3**, 53-58.—6-Mercaptopurine (I) often contains hypoxanthine (II) as a by-product and the volumetric analysis of I is then not possible. Investigation shows that I can be determined from the extinction coeff. at 325 $m\mu$ and II from the ratio of the extinctions at 258 $m\mu$ and 325 $m\mu$ in HCl soln. at pH 1. An isothermal absorption and reaction method was used for the determination of the hydrate of I. The reaction between I and water vapour was measured. It was found that the amount of water vapour reacting coincides with the theoretical value for the monohydrate.

CHEM. ABSTR.

See also Abstracts—122, Determination of chloramine T. 179, Assay of Na lauryl sulphate. 186, Determination of resorcinol. 208, Salicylates and barbiturates in serum. 209, Tolbutamide in plasma.

Food

Food and food additives, beverages, edible oils and fats, vitamins.

259. Estimation of calcium in sugar-factory products by means of the flame photometer. R. Carolan. *Int. Sugar J.*, 1959, **61**, 103-106.—Determination of Ca in beet, in syrups and juices, and in white sugar is carried out by means of a Beckman DU photometer with flame attachment No. 9200 for oxy-acetylene and blue phototube. It is shown that phosphate, if present with an excess of sulphate, does not affect the emission of Ca; K and Na are not present in sufficient quantities to interfere. *Procedure*—Dried beet (2 g) is digested with H_2SO_4 (30 ml) and 0.3 g of a selenium-graphite mixture (2:1) for 2 hr. The digest is diluted to 250 ml and 25 ml is neutralised with aq. NH_3 to methyl red. A standard is made from a calcium soln. (40 p.p.m.) containing 5% of $(NH_4)_2SO_4$. The water blank need not contain sulphate. The emission at 554 $m\mu$ is preferred for measurement and the calibration is linear from 0 to 40 p.p.m. In syrup and juices, sugar at 0.6 g per 100 ml interferes with the determination of Ca, but not with that of K or Na. The emission at 622 $m\mu$ produces rather less background. Since standards containing sugar do not keep, the reading of the water standard is multiplied by 1.2 to compensate for sugar. For thick juice (3 g per 100 ml) the water reading is multiplied by 1.4. With white sugars a 10% soln. is used, and a blank reading is made with a sugar soln. purified from metal ions by ion exchange. The results are comparable with those by EDTA determinations. E. J. H. BIRCH

260. Analysis of crude fibre. I. New process for determination of crude fibre in foods. E. Mergenthaler (Dtsch. Forschungsanst. f. Lebensmittelchem., München, Germany). *Z. Lebensmitteluntersuch.*, 1959, **109** (4), 316-321.—Analyses of 51 substances by hydrolysis with a mixture of ethanediol, water and conc. H_2SO_4 (100:10:1) are described, the process being easily reproducible. The values obtained were generally lower than those by the process of Henneberg and Stohmann (*J. Landw.*, 1859, **7**, 367), but were in adequate agreement. The described process is simpler and cheaper than those of Henneberg and Stohmann or König (*Z. Untersuch. Nahr.-u. Genussm.*, 1898, **1**, 3; 1903, **6**, 770) and can be used in serial analyses in practice. S.C.I. ABSTR.

261. Polarographic determination of nitrites in albuminous medium. V. Kureš and J. Lát (Res. Inst. Meat Industry, Prague). *Průmysl Potravin*, 1959, **10** (4), 208-213.—*Procedure*—To the sample (0.5 to 2 ml of meat brine) in a 50-ml flask add H_2O (15 ml) and heat in an atmosphere of N_2 . Prevent foaming by the addition of few drops of ethanol. When the liquid begins to boil, remove the flame, add ethanol (20 ml) and heat carefully for 5 min. to precipitate the albumins. Cool the flask and dilute the contents to vol. with H_2O . Filter and test for complete separation of albumins with 10% trichloroacetic acid soln. Transfer the filtrate (7.5 ml) to a polarographic vessel, add M KCl (0.1 ml) and methanol (1.4 ml), remove O with N_2 , add oxygen-free acetic acid (98%) (1 ml), mix carefully and immediately record the polarographic wave from -0.6 V. Compare with a calibration curve. The procedure can also be used for the determination of nitrites in various meat products after extraction with water and ethanol. J. ŽYKA

262. Determination of egg in certain foods by enzymic hydrolysis of the phospholipids. C. B. Casson and F. J. Griffin (J. Lyons & Co. Ltd., Kensington, London). *Analyst*, 1959, **84**, 281-285.—The preparation of the enzyme (lecithinase D) from white-headed-cabbage leaves is described. The sample (>6 mg of choline) is treated with acetate buffer soln. (pH 5.6) and $CaCl_2$ soln., the enzyme suspension is added and finally 0.6 ml of diethyl ether per ml of reaction mixture, which is then set aside for 16 hr. at 30°, with mechanical shaking during this period. Ether is removed from the hydrolysate, which is then diluted to 100 ml with methanol, and filtered, and the filtrate (20 ml) is run through an ion-exchange column (Zeo-Karb 225). The column is washed with water and the choline is eluted with 5 N HCl. The eluate is concentrated, adjusted to pH \approx 9.3, diluted to 60 ml, treated with ammonium reineckate and set aside overnight, together with a series of standards and a blank soln. The separated and washed ppt. of choline reineckate is dissolved in a known vol. of acetone, and its extinction is measured at 520 $m\mu$ or with Ilford 604 filters. The method has been applied to the determination of egg in ice-cream, lemon curd and salad cream and, for the purpose of determining corrections for their presence, to other phospholipid-containing food ingredients.

A. O. JONES

263. Neutral reagent for the routine determination of fat in milk and milk products. F. J. Macdonald (United Dairies Res. Lab., Wood Lane, London). *Analyst*, 1959, **84**, 287-293.—Two reagents are described. (i) The alkaline reagent is applicable without centrifuging and contains NaOH (3%, w/v), EDTA (disodium salt) (1%, w/v), NaCl (5%, w/v), n -butanol (6.25%, v/v) and industrial methylated spirit (25%, v/v). To the reagent (10 ml) in a butyrometer tube is added 10.94 ml of milk; the tube is inverted twice, placed in a water bath at 65° for 10 min., shaken, replaced in the bath and, after further inversions, the fat is allowed to rise and the reading is taken. (ii) The neutral reagent contains trisodium citrate (5%, w/v), Na salicylate (5%, w/v), EDTA (disodium salt) (1%, w/v), Tween 85 (1.1%, w/v), n -butanol (3%, v/v) and industrial methylated spirit (25%, v/v). With this reagent centrifuging is necessary after mixing, shaking and heating at 65°. Unlike the alkaline reagent, this reagent has no action on the butyrometer tubes. Applications of the neutral reagent to the determination of fat in yoghourt, cream cheese, cheese spread, condensed, evaporated and dried milk, and ice-cream are described. It is not suitable for testing separated milk.

A. O. JONES

264. Estimation of the monoglyceride content of milk. R. G. Jensen and M. E. Morgan (Storrs Agric. Expt. Sta., Conn., U.S.A.). *J. Dairy Sci.*, 1959, **42** (2), 232-239.—The methods described are based on the colorimetric determination with chromotropic acid of the formaldehyde produced by the oxidation with HIO_4 of 1-monoglycerides (I). Total monoglycerides are determined after isomerisation of 2-monoglycerides (II) to I with $HClO_4$, and the II content is then obtained by difference. The recovery of formaldehyde was quant. for monobutylin, monoolein, 1-monolaurin and 1-monopalmitin from $CHCl_3$ soln. containing 1.0 and 0.1% of purified butter fat. Normal milk was found to contain not more than a trace of I. The development of acidity in milk was accompanied, but not

paralleled, by increases in I content from 0.36 to 0.86 millimole and a II content from 0.56 to 0.99 millimole per 100 g of fat. The presence of diglycerides in rancid milk is indirectly indicated.

W. H. C. SHAW

265. Proposed method for the rapid determination of lactose in separated milk and condensed whey by infra-red absorption. J. D. S. Goulden (Nat. Inst. Res. Dairying, Shinfield, Reading, England). *J. Dairy Res.*, 1959, **26** (2), 151-156.—The method described is based on the measurement of the extinction at 1040 cm^{-1} for separated milk or at 1040 , 1117 or 1155 cm^{-1} for condensed whey, the lower casein content of which permits the use of the last two weak extinctions. Cells 10 to $62\text{ }\mu$ thick, with BaF_2 windows, are used. On separated milk an error up to $\pm 1.5\%$ of the lactose concn. may occur, and condensed whey samples with lactose concn. up to 35% can be assayed within $\pm 8\%$, using the weaker absorption bands.

W. H. C. SHAW

266. Detection of adulteration of human milk with cows' milk by paper electrophoresis. M. Padmoyo and O. Högl (Lab. des Eidg. Gesundheitsamtes, Bern). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (2), 110-119.—The main constituent of the protein of human milk is albumin, that of cows' milk is casein. These proteins can be separated by paper electrophoresis of the buffered sample (phosphate buffer, pH 6.2), without preliminary treatment, at 20° with a p.d. of 220 V . Extinction curves are plotted for the length of the strip and are characteristic of the protein. The addition of 5% of cows' milk can be detected from the change in the extinction curve by the method of calculation described.

G. BURGER

267. Investigation of the proteins of cows' milk by paper electrophoresis. E. A. Zhadnova and I. N. Vlodavets (All-Union Sci. Res. Inst. of the Dairy Ind., Moscow). *Biokhimiya*, 1959, **24** (3), 398-403.—Whey proteins, obtained by the removal of casein from skimmed milk by pptn. at the isoelectric point, were concentrated by salting-out with $(\text{NH}_4)_2\text{SO}_4$ and subsequent dialysis of the ppt. By paper electrophoresis a distinct partition of the proteins was obtained within 18 hr. in a barbitone buffer (pH 8.6, ionic strength 0.1) on $4\text{ cm} \times 40\text{ cm}$ strips at 150 to 350 V . Four fractions were obtained, viz. serum albumin (4.3%), β -lactoglobulin (60.2%), α -lactalbumin (20.4%) and immune globulins (15.1%); colostrum whey on the first day of lactation contained over 80% of immune globulins. Casein proteins were partitioned in a similar buffer to which 40% of urea had been added to facilitate the break-down of hydrogen bonds and thereby prevent aggregation and complex-formation. Within 18 hr. on $4\text{ cm} \times 55\text{ cm}$ strips at 150 to 320 V , three distinct fractions were obtained, viz. α -casein (36.6%), β -casein (56.9%) and γ -casein (6.5%). Tests showed that, in a buffer containing 40% of urea, artificial mixtures of α - and β -casein could be quant. partitioned without any complex-formation. It is suggested that previous figures for α -casein were high owing to a complex containing approx. equal amounts of α - and β -casein being counted as pure α -casein. K. R. C.

268. Standardisation of the Harland-Ashworth test for whey-protein nitrogen. S. Kuramoto, R. Jenness, S. T. Coulter and R. P. Choi (Minnesota Univ., St. Paul, U.S.A.). *J. Dairy Sci.*, 1959, **42** (1), 28-38.—The test (cf. *Food Res.*, 1947, **12**, 247)

is modified in that standard curves relating turbidity to the whey-protein N content are prepared by using appropriate mixtures of salt filtrates prepared from two lots of defatted dried milk, one containing a low, and the other a high, level of undenatured whey protein. From the results of a collaborative study it is concluded that the modified test is of sufficient precision to form the basis of specifications for dried skimmed milk.

W. H. C. SHAW

269. Changes in the paper-electrophoretic whey-protein pattern of cows with acute mastitis. J. G. Lecce and J. E. Legates (N. Carolina State Coll., Raleigh, U.S.A.). *J. Dairy Sci.*, 1959, **42** (4), 698-704.—From a study of the effects of mastitis on the whey-protein electrophoresis pattern it is concluded that the appearance of a fraction migrating as blood-serum albumin is a reliable indication of inflammation, and hence of mastitis. Relative increases in the proportion of immune globulins were also noted.

W. H. C. SHAW

270. Milk test for ketosis in dairy cows. L. H. Schultz and M. Myers (Wisconsin Univ., Madison, U.S.A.). *J. Dairy Sci.*, 1959, **42** (4), 705-710.—The level of the acetoacetic acid-acetone fraction of the milk, determined colorimetrically after pptn. of proteins and distillation, is considered a reliable indication of the degree of ketosis, assessed both by a commercial qual. test (Na_2CO_3 , $(\text{NH}_4)_2\text{SO}_4$ and sodium nitroprusside) and by the external symptoms of ketosis. The correlation coeff. (on 80 samples) between the milk and blood levels for this fraction was $+0.87$. For the β -hydroxybutyric acid fraction the lower coefficient ($+0.36$) is attributed to mammary utilisation of this compound.

W. H. C. SHAW

271. Study of the fatty-acid composition of the Reichert-Meissl and Polenske fractions of butter fat and its admixtures with other fats. A. Sengupta (Cornell Univ., Ithaca, N.Y.). *Dissert. Abstr.*, 1959, **19** (9), 2204.—Chromatography of the Reichert-Meissl fraction of a sample of butter fat showed it to contain 65.3% of butyric, 30.1% of n -hexoic and 4.6% of n -octoic acids; the Polenske fraction contained 0.6% of butyric and n -hexoic, 22.1% of n -octoic, and 76.7% of n -decoic and higher acids. n -Octoic acid is thus divided between the 2 fractions. The adulteration of butter with fats of low Reichert-Meissl and Polenske values caused decreases in both the butyric and the hexoic-octoic acid groups. Adulteration with coconut fat (Reichert-Meissl fraction, 27.5% of n -hexoic and 72.5% of n -octoic acid, Polenske fraction 54.5% of n -octoic and 45.5% of n -decoic and higher acids) caused a decrease in the butyric acid content; the total content of n -hexoic and n -octoic acids remained constant, but n -octoic acid increased and n -hexoic acid decreased. Cooling the Reichert-Meissl-Polenske distillate to 6° for 20 min. caused solidification of the Polenske fraction and an increase in the Polenske value equal to the loss of acidity in the Reichert-Meissl fraction and in the wash water, n -octoic acid being responsible for this change.

M. D. ANDERSON

272. Isolation and identification of the high-molecular-weight saturated fatty acids of butter fat. R. P. Hansen, F. B. Shorland and N. J. Cooke (Dept. Sci. Ind. Res., Wellington, N.Z.). *J. Dairy Res.*, 1959, **26** (2), 190-195.—By fractional crystallisation methods applied to the fatty acids and their methyl esters the presence in New Zealand

butter fat of normal C_{18} , C_{21} and C_{23} odd-numbered and normal C_{18} , C_{22} , C_{24} and C_{26} even-numbered fatty acids is confirmed. *n*-Eicosanoic acid (C_{20}) has been isolated and identified by its chemical and physical properties.

W. H. C. SHAW

273. Microbiological detection of preservatives other than benzoic or sorbic acid in margarine with a sodium chloride-tolerant yeast as test strain. G. Eijgelaar and D. A. A. Mossel (Central Inst. for Nutrition and Food Res. T.N.O., Utrecht, The Netherlands). *Analyst*, 1959, **84**, 293-296.—The organism used is *Candida brumptii* isolated from river water by an enrichment procedure. Since it is only weakly saccharolytic, impaired growth is the measure of inhibition. Serum (10 ml) is obtained from margarine by heating at $43^{\circ} \pm 1^{\circ}$, its NaCl content is determined and adjusted to 9% with sterile NaCl soln. or water, and to it are added soln. of yeast extract and glucose, and the pH is adjusted to 6.9. The inoculum is a sub-culture of the organism in a glucose-yeast extract-NaCl medium incubated for 24 hr. at 30° , and its content of viable cells per ml is determined. A dilution of the culture is mixed with 2 ml of the adjusted and filtered sterile serum and 1 ml of sterile 4.5% aq. agar, in duplicate culture tubes set almost horizontally, and these are then incubated for 48 hr. at 30° with two similarly inoculated blank tubes containing an agar medium and 0.3% of Na benzoate. The number of colonies developing in the four tubes is determined, and growth is considered to be inhibited when the number on an average sample strip is 10% or less of the average number in the blank strip. Sorbic acid does not interfere. Limits of detection of certain antimicrobial agents are quoted.

A. O. JONES

274. Analysis of coffee mixtures. H. Gál (Stadt. Anst. f. Chem. u. Lebensmitteluntersuch., Budapest, Hungary). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (2), 57-76.—In ground mixtures of coffee with chicory and other coffee substitutes, the coffee content can be estimated by determination of the fat content. Coffee contains approx. 14.1% of fat, while the substitutes contain from 2 to 2.4% of fat. The fat is extracted by shaking with diethyl ether and weighed. A graph shows the relation between the fat content and the coffee content of the mixture. In decoctions containing more than 50% of coffee, the coffee is determined by the determination of chlorogenic acid by the colorimetric method of Plücker and Keilholz, in which a dil. aq. extract is treated at 8° with NaNO_2 and NaOH soln., and the intensity of the resulting colour is referred to a curve prepared from known mixtures of coffee. Chicory is determined by means of its fructose content (Seliwanoff's reaction). Cereals in coffee have an average starch content of 13.5% and are determined by the iodine-starch reaction.

G. BURGER

275. Spectrofluorimetry of edible oils. II. F. De Francesco (Staz. Sper. Agr. San. Michele dell'Adige, Trento, Italy). *Olii Min.*, 1959, **36** (3), 73-76.—The effects of de-acidification, decolorisation with active carbon or alumina, and the addition of adulterants on the fluorescence spectrum of olive oil have been examined and the spectra obtained are given.

L. A. O'NEILL

276. Applications of spectrophotometry in the analysis of olive oil. Use of ultra-violet spectrophotometry for the characterisation of superfine

virgin olive oil. II. A. Montefredine and L. Laporta (Lab. Chim. Provinciale di Pescara, Italy). *Olii Min.*, 1959, **36** (3), 63-72.—A u.v. spectrophotometric examination was made of 206 samples of olive oil, 17 of which were refined or commercial and 189 were genuine pressed oils. Of the latter, 40 were rancid (Kreis or peroxide tests), 28 were acid (>3% of oleic acid), 36 were acid and rancid, 40 were classified as fine and 45 as superfine. The K ($= E_{1\%}^{1\text{cm}}$) values at 232, 262, 264, 268, 270, 272, 274 and 280 μ are reported and the ratios R ($= K_{232}/K_{270}$) and ΔK [$= K_{268} - 0.5(K_{264} + K_{274})$] calculated. Both the R and ΔK values were related to the quality of the oil. Thus, of the 85 fine or superfine oils only 3 had an R value of <10, whereas most of the acid, rancid or commercial oils had R values of <10. The ΔK value was positive for 60% of the fine oils and 24% of the superfine oils, with average values of 9.02 and 4.70, respectively. Most of the other oils had much higher positive ΔK values.

L. A. O'NEILL

277. Characterisation of the carboxylic acids used in the fat and soap industries by oxidation with chromic acid. M. Jureček and P. Kozák (Chem.-Tech. Hochschule, Pardubice, CSR). *Z. anal. Chem.*, 1959, **167** (1), 32-38.—The procedure permits the characterisation and differentiation of fatty, naphthenic and resin acids. Weighed samples of typical acids were oxidised with a chromic-sulphuric acid mixture under the conditions described by Kuhn and Roth (*Ber.*, 1933, **60**, 1274). The reaction mixture was steam-distilled and the volatile acids were titrated with KOH soln. The alkali required, expressed as mg of KOH necessary to neutralise the acids from 1 g of starting material, was designated the "Kuhn-Roth Number." The ratio of this value to the corresponding acid value is characteristic of the type of acid, and is <1 for the fatty and resin acids, and >1 for naphthenic acids. A further difference is that the fatty acids give a turbid steam-distillate, while the naphthenic and resin acids give clear distillates. Results obtained for 16 typical acids are tabulated and discussed. The volatile acids from the materials were identified by paper chromatography of the ethylammonium salts.

S. M. MARSH

278. Quantitative determination of ascorbic acid in vegetable extracts with special reference to polarography. H. Woggon. *Ernährungsforschung*, 1959, **4** (1), 35-43.—A review of methods for the determination of ascorbic acid, applicable to the analysis of vegetable extracts, is given. (42 references.)

G. P. COOK

279. Complete analysis of tocopherol mixtures. I. Introduction and an investigation into differential coupling reactions. J. Green and S. Marcinkiewicz (Walton Oaks Exp. Sta., Vitamins Ltd., Tadworth, Surrey, England). *Analyst*, 1959, **84**, 297-303.—Attempts are made to combine methods based on differential coupling reactions with paper chromatography to effect the separation of β - from γ -tocopherol and ϵ - from η -tocopherol. The reactions of the four tocopherols with diazotised *o*-dianisidine and with a new reagent, viz. 2,6-dichloro-*p*-benzoquinone-4-chlorimine (Gibbs's reagent), are studied. It is shown that β - and ϵ -tocopherols are oxidised in the presence of these reagents and that the recovery with either reagent is not quant. Neither of these coupling reactions can therefore form the basis of an analytical method.

II. Separation of nitrosotocopherols by paper chromatography and their determination. S. Marcinkiewicz and J. Green. *Ibid.*, 1959, **84**, 304-312.—The sample ($>600 \mu\text{g}$) of the mixture of β - and γ -tocopherols or of ϵ - and η -tocopherols, dissolved in 5 ml of ethanol, is treated with 0.2 ml of acetic acid, 3 ml of NaNO_2 soln. (2%) and, after exactly 90 sec., with 2 ml of KOH soln. (20%). Water (10 to 15 ml) is added and the nitrosotocopherol is extracted with light petroleum. The extract is washed with water and evaporated under reduced pressure at 30° , and the residue is dissolved in 1 ml of light petroleum. This soln. is chromatographed on paper impregnated with liquid paraffin, with 93% (v/v) ethanol as the ascending phase. The yellow bands are cut out and eluted separately with ethanol (3 ml) and the nitrosotocopherols are determined by a modified Emmerie-Engel method, the extinctions being measured after 60 min. In the chromatography of small amounts of nitrosotocopherols ($\approx 5 \mu\text{g}$), the paper is first impregnated with ZnCO_3 and fluorescein sodium, the latter to render the spots visible in u.v. light. Recovery experiments gave good results. Applications of the method to determinations in maize, rice and cottonseed oils are described. A. O. JONES

See also Abstracts—42, Determination of Sr in milk. **84**, Determination of NO_2^- in food. **154**, Determination of Ni in oils. **181**, Determination of bromoacetic acid. **193**, Detection of sorbic acid.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

280. New portable apparatus for the automatic analysis of air in factories. S. Kündig. *Chimia*, 1959, **13** (3), 84-88.—The apparatus automatically measures the concn. of toxic substances in the atmosphere. The air is aspirated through a quartz pyrolysis tube heated to 800° to 1000° , and then through a reaction vessel containing H_2O , the change in resistance of the resulting soln. being measured with a Wheatstone-bridge circuit, and plotted on a recorder; alternatively, an alarm system can be operated through a suitable relay. The total vol. of air for each determination can be varied by altering (electronically) the time of aspiration. The period between measurements is similarly controlled, and the reaction vessel is emptied and refilled by means of magnetic valves. Substances that can be measured include (i) trichloroethylene and other aliphatic halogenated compounds; the HCl first formed is oxidised to COCl_2 ; (ii) mono- and di-chlorobenzenes, which are converted into HCl and COCl_2 ; (iii) CS_2 and H_2S , which are converted into SO_2 ; and (iv) aromatic hydrocarbons; the air containing these is passed through an ozoniser, thence to the apparatus; oxalic acid is the end-product. As little as 20 p.p.m. can be measured. H. M.

281. Determination of trace amounts of methane in air. D. M. G. Lawrey and C. C. Cerato (Res. and Engng Dept., Sun Oil Co., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1011-1012.—From 1 to 6000 p.p.m. by vol. of methane (I) in air can be determined by a gas-chromatographic procedure in which a high-sensitivity amplifier and a splitter column packed with partially deactivated charcoal are used to obtain the desired

sensitivity and resolution. The results on 11 standard blends ranging from 15 to 6000 p.p.m. of I gave an average deviation of $\pm 11\%$. At the 30 p.p.m. level the standard deviation was ± 2.37 p.p.m. (8 determinations). K. A. PROCTOR

282. New indicator for the mercurimetric chloride determination in potable water. E. Goldman (San. Engng Div., Dept. of Water and Power, Los Angeles, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1127.—The modified indicator is prepared by dissolving cryst. diphenylcarbazone (0.25 g), conc. HNO_3 (4 ml) and Xylene cyanol FF (C.I. Acid Blue 147) (0.06 g) in 95% ethanol (100 ml). The soln. is stable for two months if kept at 0° in a dark bottle. *Procedure*—To an aliquot of the sample soln. ($\text{Cl}^- < 10 \text{ mg}$) add exactly 1 ml of indicator to bring the pH value to the optimum (2.5 ± 0.2) for the titration. Titrate with standard $\text{Hg}(\text{NO}_3)_2$ soln. to a sharp purple end-point, and for the blank titrate 100 ml of distilled H_2O containing Na_2CO_3 (10 to 20 mg). W. J. BAKER

283. Determination of radioactivity due to caesium, strontium, barium and cerium in waters and filters. R. G. Osmond, M. J. Owers, C. Healy and A. P. Mead [U.K.A.E.A. (Res. Group), Royal Arsenal, Woolwich, London]. A.E.R.E. Report AERE-R2899, 1959, 39 pp.—Modifications to a previous method (cf. Osmond *et al.*, *Anal. Abstr.*, 1958, **5**, 2013) for the analysis of rain-water are described. The method has been applied to tap-water and rain-water (100 litres); special steps ensure the elimination of K in the separation of ^{137}Cs . Air filters made from esparto-grass paper are ashed with carriers and then subjected to an alkaline fusion or to treatment with acid; the latter treatment is generally preferred; the separations of the radioactive nuclides are the same as those for the water samples. Full details of the counting and calculation procedures are given. The limit of detection of any nuclide is $\approx 1 \mu\text{C}$. G. J. HUNTER

284. Conductimetric determination of the total salt content of boiler water. J. A. de Nooyer and G. B. Smit (N.V. tot Keuring van Electrotech. Materialen, Arnhem, Netherlands). *Chem. Weekbl.*, 1959, **55** (14), 150.—In this determination it is necessary to eliminate OH^- from the sample, since their mobility differs appreciably from those of other ions present. The use of gallic acid for this purpose gives non-reproducible results owing to the conductivity of the excess of gallic acid. Pyrogallol, which has a smaller dissociation constant than gallic acid, is a more suitable reagent. M. J. MAURICE

See also Abstract—25, Determination of Na in water.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

285. Estimation of the trace-element status of large areas of soil. A. C. Oertel (Div. of Soils, C.S.I.R.O., Adelaide, Australia). *Aust. J. Agric. Res.*, 1959, **10** (1), 58-70.—A statistical method is described which involves chemical determinations on a small number of soil samples only. From these analyses a value for the median concn. of any element is derived. The average change in concn. with

depth, defined as the trend (T), is obtained from the equation $W = S/(1 - T)$; (W is the weighted mean concn., S is the concn. of the surface sample). The validity of the results obtained can be tested by Pitman's method (*Suppl. J. R. Statist. Soc.*, 1937, **4**, 119). The greatest difference in concn. of one element within one profile is defined by the variability (V), which can be obtained from the equation $(H - L) = VS/(1 - T)$; (H is the lowest concn. and L is the highest concn. in the profile). The statistical method has been applied to 25 profiles of Australian soil. S. BAAR

286. Separation and determination of total copper and zinc in soil. P. F. Pratt and G. R. Bradford (Univ. Calif. Citrus Exp. Sta., Riverside, U.S.A.). *Proc. Soil Sci. Soc. Amer.*, 1958, **22**, 399-402.—The soil sample (1 g, 100 mesh) is fused with Na_2CO_3 (3 g), and the melt is dissolved in N HCl (100 ml). The soln. is evaporated to dryness, 20 ml of 3 N HCl is added and the evaporation repeated. The residue is heated with a further 20 ml of 3 N HCl and the soln. filtered through a paper (previously washed with 3 N HCl) into a 50-ml flask, the ppt. being washed free from Fe^{3+} before the soln. is diluted to the mark. An aliquot of the soln. (containing Cu 2.5 to 5 μg , Zn 5 to 100 μg , and Fe ≥ 35 mg) (or the equiv. of 0.5 g of soil) is passed through a column (36 cm \times 0.9 cm) of Dowex-1 resin (V-10, 200 to 400 mesh) previously washed successively with conc. HCl , aq. HCl (1:1), aq. HCl (1:5) and water. The test soln. is followed by 15 ml of 3 N HCl and, after draining the eluate (discarded), more 3 N HCl is added until the coloured zone due to Fe reaches the lower end of the column or until 100 ml of eluate has been collected. Copper in the eluate is determined by the zincon method; Fe is removed from the column by washing with 100 ml of N HCl followed by 20 ml of N KCl ; Zn is then eluted with 35 ml of 0.001 N HCl and determined by the zincon method. A. G. POLLARD

287. Determination of very small amounts of magnesium for agricultural chemical analyses. K. Scharrer and K. Mengel (Univ. Giessen, Germany). *Z. Pflernähr. Düng.*, 1957, **77**, 18-36.—A titrimetric method, involving the pptn. of Mg with 8-hydroxyquinoline (I), and a flame-photometric method were investigated for determining Mg in plant materials and soil extracts. The pptn. of Mg with I in NaOH -tartrate buffer is quant. at pH 10.0 to 10.8; Fe and Ca must be removed. Dissolve the ppt. in 3 N HCl , add KBr , and titrate with an excess of KBrO_3 soln. Determine the exact end-point by adding KI and back-titrating with $\text{Na}_2\text{S}_2\text{O}_3$ soln. Satisfactory results were obtained on plant-tissue samples containing 2 to 10 mg of Mg, but not with 0.1 to 0.5 mg. Use a flame photometer with photomultiplier to observe the 3710-Å line for soln. containing 0 to 50 p.p.m. of Mg. At this wavelength K, Na and Ca increased the emission, and SO_4^{2-} and PO_4^{3-} decreased it. From plant-tissue digests, remove the interfering cations by pptn. as sulphates in ethanol and the anions by passage through an anion-exchange resin. Soil extracts obtained with 0.025 N CaCl_2 for determining available Mg could be analysed without removal of interfering ions. CHEM. ABSTR.

288. Orange I method for determining soil nitrates and a comparison with the phenolsulphonic acid method for certain soils of Northern Nigeria. K. R. Middleton (Rubber Res. Inst., Kuala Lumpur, Malaya). *J. Sci. Food Agric.*, 1959, **10** (4), 218-224.—In the colorimetric method described, the NO_3^-

are reduced to NO_2^- with zinc at pH 10 to 11 in the presence of Mn^{2+} ; the NO_2^- are then diazotized with sulphanilic acid and coupled with 1-naphthol to give 4-*p*-sulphophenylazo-1-naphthol (Orange I) (C.I. Acid Orange 20). The method, which is sensitive to 0.006 p.p.m. of nitrate N and has a precision of $\approx 3\%$, is much quicker than the previous phenolsulphonic acid method. On oven-dried samples the loss of NO_3^- as measured by the Orange I method is only a third of that measured by the other method. On air-dried samples the Orange I method gives slightly lower results for high values of NO_3^- and higher results for low values; this last finding is probably due to the much lower sensitivity of the phenolsulphonic acid method. *Procedure*—The sample (10 g) of air-dry soil is treated with 50 ml of an ammoniacal Ca acetate soln. (0.5% of anhyd. Ca acetate, free from NO_3^- , in 4% aq. NH_3) and 1 ml of Mn^{2+} soln. (1% of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in 5% aq. acetic acid). A pinch of finely divided zinc is added, and the soln. is shaken for ≈ 5 min.; 20 ml is immediately filtered off and treated with 5 ml of reagent containing 0.1% of sulphanilic acid and 0.08% of 1-naphthol in 75% aq. acetic acid. After 30 min. the extinction is measured in a 2-cm cell at 475 $\text{m}\mu$. J. H. WATON

289. Radio-assay of uranium and plutonium in vegetation, soil and water. E. L. Geiger (E. I. du Pont de Nemours and Co., Aiken, S.C.). *Health Phys.*, 1959, **1**, 405-408.—The assay is based on the extraction of U and Pu from 4 to 6 N HNO_3 into 50% tributyl phosphate in *n*-tetradecane. Uranium and Pu are recovered together with sufficient reduction in total solids to allow α -counting and pulse-height analysis. Data from several hundred "spiked" samples to which U and Pu were added indicate a nearly equal recovery of U and Pu. Average recoveries are $76 \pm 14\%$ for vegetation, $76 \pm 16\%$ for soil, and $82 \pm 15\%$ for water. The procedure is designed for samples that may be collected and analysed for radioactivity as a part of a health-physics regional-monitoring programme. NUCL. SCI. ABSTR.

290. Determination of Phosdrin in vegetables. E. Q. Laws (Dept. of the Gov. Chemist, Clement's Inn Passage, Strand, London). *Analyst*, 1959, **84**, 323-324.—Laws and Webley's method (*Analyst*, 1959, **84**, 28) for determining demeton-methyl by the photometric measurement of H_2PO_4^- after a chromatographic separation may be applied to Phosdrin (I) (a mixture of *cis*- and *trans*-isomers of 2-methoxycarbonyl-1-methylvinyl dimethyl phosphate) without modification if care is taken to avoid volatilisation of the insecticide during evaporation of the CHCl_3 extract. Gentle heat in a current of air suffices. When a dil. soln. of the insecticide of known purity was added to raw cabbage, recoveries were $\approx 90\%$. The results of field tests are given, samples being taken 1.5 to 168 hr. after spraying. Determinations by anticholinesterase measurement were made with some samples, and lower results obtained in the later stages by this method suggest that the more active isomer is decomposed before the less active. If samples are kept in a refrigerator, I is decomposed by the plant material, but with storage in deep-freeze there is no loss. Although I is rapidly decomposed by plant material it has high mammalian toxicity. A. O. JONES

See also Abstracts—25, Determination of Na in soil. 42, Determination of Sr in plants. 149, Determination of Co in soil.

5.—GENERAL TECHNIQUE AND APPARATUS

General

291. Slide-rule for converting percentages to mole fractions. C. R. Masson (National Res. Council, Halifax, N.S., Canada). *Anal. Chem.*, 1959, **31** (6), 1122-1124.—The slide-rule described has been developed specifically for the components of basic open-hearth slags and may be constructed from any slide-rule which has an L scale and an inverted D scale on the body. Circular scales, which are also described, offer several advantages.

K. A. PROCTOR

292. Apparatus for the colorimetric determination of trace components in gases. Z. Łada and S. Waszak (Inst. Gen. Chem., Warsaw). *Rev. Chim., Bucharest*, 1959, **10** (3), 162-165.—Apparatus is described and illustrated for the continuous determination of traces of O or Cl in gases. The determination of O depends on the oxidation of a weakly alkaline soln. of alizarin red S and comparison of the reduction in colour with that produced by a known amount of O generated electrolytically. For the determination of Cl the liberation of iodine from KI soln. and measurement of the colour is used. It is claimed that the apparatus will detect <0.01% of O. It can also be used for the determination of CO₂, N, O₂, SO₂ and H₂S.

H. SHER

293. Determination of reflux ratio and boil-up rate for distillation column with intermittent take-off-type reflux control. Yi-Chung Chang and Liang-Tseng Fan (U.S. Bureau of Mines, Morgantown, W. Va.). *Anal. Chem.*, 1959, **31** (6), 1121.—With the procedures described, and the reflux-regulating device of Brandt *et al.* (*Oil Gas J.*, 1946, **45**, 86, 102) accurate reflux ratios can be easily determined and controlled.

K. A. PROCTOR

294. Weight burettes. F. L. Hahn (Angel Urraza 718-303, Mexico 12, D.F.). *Z. anal. Chem.*, 1959, **167** (2), 104-105.—A polyethylene squeeze-bottle is modified to form a weight burette. The usual delivery tube is removed and a fine curved plastic tube is substituted. This tube, which must be an air-tight fit in the stopper, extends just inside the bottle and, by tilting and squeezing, a small drop of liquid can be expelled. The loss in weight is rapidly and conveniently measured by means of a damped automatic loading balance to 0.1 mg. The loss in weight of the burette on standing is not more than 4 mg per hr. The plastic sheath of a low-voltage wire is suggested as a suitable fine tube.

H. M.

See also Abstract—280, Apparatus for automatic analysis of air.

Chromatography, ion exchange, electrophoresis

295. Analytical applications of a Celite-dinitrophenylhydrazine column. P. H. Begemann and K. de Jong (Unilever Res. Lab., Vlaardingen, Netherlands). *Rec. Trav. Chim. Pays-Bas*, 1959, **78** (4), 275-283 (in English).—Carbonyl compounds (≈ 0.5 mg) in soln. in light petroleum are quant. converted into 2:4-dinitrophenylhydrazones by passage through a column (27 cm \times 1 cm) of Celite (15 g) impregnated with a soln. of 2:4-dinitrophenylhydrazine (50 mg) in 2 N HCl (7.5 ml). To locate double bonds in unsaturated hydrocarbons

and fatty acid esters, add a 0.1 M soln. of the sample in CCl₄ (20 μ l) to a satd. soln. of ozone in CCl₄ (1 ml), and after 15 min. remove the excess of ozone by passage of N₂; add light petroleum (1 ml), transfer to the column, elute with light petroleum and identify monohydrazones in the eluate by the paper-chromatographic method of Klein and de Jong (*cf. Anal. Abstr.*, 1957, **4**, 2639). Bis-hydrazones resulting from dicarbonyl products of ozonolysis are insol. in light petroleum, but may be eluted with dioxan.

A. R. ROGERS

296. Versatile electronic device for counting drops of eluent in chromatography or operating ancillary apparatus after pre-set counts or pre-set times. G. L. Reed and H. Irving (Inorg. Chem. Lab., South Parks Road, Oxford). *Analyst*, 1959, **84**, 317-320.—The electronic device described has three selector dekadrons, and was constructed primarily to count drops of effluent falling from an ion-exchange column and to operate such apparatus as a sample-changer after a pre-selected number of drops, up to 1000, has been counted. It is suitable for the collection of small sample volumes, but the volume can be varied from ≈ 0.05 to 50 ml even during elution. It can also be used as an interval timer to operate external circuits at regular intervals.

A. O. JONES

297. Chromatographic investigations. XII. The application of differential polarography to the determination of the concentration of the eluate flowing from chromatographic columns. W. Kemula, S. Brzozowski and K. Butkiewicz (Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 489-494.—A pair of chromatographic columns is used for the determination of the concn. of the eluate, one being used for a standard soln. and the rate of flow in both columns being identical. The potential is measured on a galvanometer and compensation is made for the diffusion currents due to the O present.

H. DMOWSKA

298. Paper-disc column chromatography. L. Roth (Lab. de Firma Carl Roth, Karlsruhe, Germany). *Mikrochim. Acta*, 1959, (4), 582-585 (in German).—Chromatographic columns consisting of superimposed thick paperboard discs can be used for purification purposes. The material in the column can be located by spraying, or individual discs can be removed and purity tests carried out on them. The columns can be lengthened during the operation, and quant. chromatographic determinations are possible. Diagrams of the apparatus are given.

G. P. COOK

299. Improvement in ascending paper-strip chromatography. A. Blumenthal (Chem. Lab. der Stadt, Zürich). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (2), 83.—The paper strip is suspended from a hook in a glass cylinder and has a glass weight attached to the lower end. The weight is wider than the strip, and enables the strip to hang tautly without touching the container.

G. BURGER

300. Quantitative evaluation of paper chromatograms. A. R. Neurath and F. Frič (Dept. Plant Physiol., Biol. Inst. Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1959, **13** (4), 247-253.—The evaluation is carried out by means of the microphotometric measurement of negatives obtained by photographing the chromatograms with the use of coloured filters. The errors caused by the non-uniform structure of the paper can be thus avoided,

spots with unstable colouration can be photographed immediately during the detection of the chromatograms, spots of irregular diffusion character can be measured and, by the use of colour (interference) filters, spots detected with similarly coloured reagents can also be evaluated.

J. ŽYKA

301. Automatic scanner for electrophoresis and chromatography paper strips. G. Smilanić and T. Rabuzin (Inst. "Rudjer Bošković," Zagreb, Yugoslavia). *J. Sci. Instrum.*, 1959, **36** (1), 160-163.—The device automatically records the extinction, the integral of the extinction, the radioactivity intensity and the integral of the radioactivity intensity as a function of the position of the paper strip. Electronic circuits are described.

G. SKIRROW

302. Gas chromatography. I. Powerful new tool for chemical analysis. H. H. Hausdorff and N. Brenner (Perkin-Elmer Corp., Norwalk, Conn., U.S.A.). *Oil Gas J.*, 1958, **56**, 73-75.—A brief discussion of basic principles is given.

II. Instrumentation techniques play a vital role in chemical analysis by gas chromatography. H. H. Hausdorff and N. Brenner. *Ibid.*, 1958, **56**, 122-124.—The selection of detector, carrier gas and column packing is discussed.

III. Six variables must be considered for effective gas chromatography. H. H. Hausdorff and N. Brenner. *Ibid.*, 1958, **56**, 86-88.—The effect of flow rate, pressure, temp., column dimensions, solid support and partition liquid on the running speed, separation and quant. accuracy is discussed for the eight-component mixture pentane-acetone- CS_2 -dichloromethane-ethyl acetate-cyclohexane- CCl_4 -benzene. General considerations are given for choosing the best partition liquid for any separation.

IV. Limits in application for gas chromatography. H. H. Hausdorff and N. Brenner. *Ibid.*, 1958, **56**, 89-90, 93-96.—The qual. aspect of gas chromatography is expressed as retention time, retention ratio or retention vol. The method is rendered quant. by means of internal normalisation, internal standard, or peak-height calibration. Trace analysis techniques are discussed, and possible uses of gas chromatography to obtain fundamental physical and chemical data are outlined.

CHEM. ABSTR.

303. A sample-injection method for gas-liquid chromatography. F. G. Stanford (U.K.A.E.A., Radiochem. Centre, Amersham, Bucks., England). *Analyst*, 1959, **84**, 321-322.—The simple apparatus described removes difficulties associated with the use of a syringe and is particularly useful when the amount of sample available is limited and also when the sample is toxic or radioactive. A rubber stopper carrying a glass delivery-tube terminating in a jet (1 mm bore) replaces the vaccine cap that normally closes the top of the column. The delivery tube is closed by a rubber stopper. This stopper can be replaced by a similar one carrying the sample capillary tube, the end of which passes through the jet in the delivery tube and touches the top of the column. The capillary tube has a micro bulb by means of which the sample is drawn into the tube, which is then weighed and fitted into the column, where it remains, after discharging the sample, until the end of the run. It is then reweighed. Samples from 1 to 100 mg can be used and a graph of peak size vs. sample wt. is linear.

A. O. JONES

304. Potentiometric control of the separation of acids on ion-exchange columns. W. Czerwiński (Dept. of Anal. Chem., Inst. of Gen. Chem., Warsaw). *Chem. Anal.*, Warsaw, 1959, **3** (3-4), 475-482.—A silver-silver chloride and glass electrode system with automatic potentiometric registration is used for measurements on the eluate as it flows from the column. The method is applied for checking the separation of H_2SO_4 from formic and acetic acids. Graphs showing the change of potential during the separation are given.

H. DMOWSKA

Optical

305. Flame photometry. I. G. Pietzka and H. Chun (Anal. Lab., Farbwerke Hoechst A.-G., Frankfurt a.M.). *Angew. Chem.*, 1959, **71** (8), 276-283.—Sources of error in flame photometry are discussed in detail and methods for their elimination are proposed. Errors due to changes in the ionisation or dissociation equilibria or to the formation of not readily excitable compounds are overcome by a "substitution method," especially suitable for the alkaline-earth metals. Various amounts of an extraneous element (e.g., Sr or Ba for the determination of Ca at 423 m μ) are added so as to keep the emission intensity directly proportional to the amounts of the element to be determined in the sample (used in successive dilutions). Thus the extraneous element is "substituted" for that determined and compensates for the (negative) errors normally due to general interference. Empirically, for each 1 μg of Ca, 2 μg of Sr and 3-5 μg of Ba are required. The increased intensity leads to increased sensitivity. The method, with suitable extrapolation on calibration curves, works well on synthetic mixtures of Ca (30 μg) in the presence of PO_4^{3-} (10 μg), Al (50 μg) and Ti (100 μg).

J. P. STERN

306. The tape machine. I. A new tool for spectrochemical analysis. A. Danielsson, F. Lundgren and G. Sundkvist (Res. Lab., Boliden Mining Co., Skelleftehamn, Sweden). *Spectrochim. Acta*, 1959, (2), 122-125.—The sample in powder form is deposited uniformly by a mechanical device on to an adhesive tape, which is passed through the spark gap between two graphite electrodes. In this way new material is continuously fed to the spark and it is claimed that changes in line intensities with time are minimised and greater precision is attained. The device is described in detail and may be used in direct-reading or ordinary spectrographic work.

II. Applications using different kinds of isoformations. A. Danielsson and G. Sundkvist. *Ibid.*, 1959, (2), 126-133.—A detailed description is given of the methods used to convert various types of sample into a uniform state with respect to particle size and chemical and mineral composition. The treatments include simple grinding, and grinding after the addition of buffers, or dissolution followed by evaporation to dryness, or separation by ion exchange, or chemical pptn. of the elements concerned, or fusion. Comparative results obtained with the new technique and by chemical analysis show good agreement for the determination of Cu, Zn and Pb over the range 1 to 30%. The method is suitable for ores, concentrates, tailings, slags and other smelter products.

III. Notes on useful corrections in spectrochemical analysis with the tape technique. A. Danielsson

and G. Sundkvist. *Ibid.*, 1959, (2), 134-137.—The methods of applying corrections for background variations and self-absorption are described. In some applications of the tape-machine technique, a useful improvement in the coeff. of variation by a factor of 2 or more is obtained. P. T. BEALE

307. The plasma jet as a spectroscopic source. M. Margoshes and B. F. Scribner (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *Spectrochim. Acta*, 1959, (2), 138-145.—The excitation conditions available from a normal spectroscopic d.c. arc source, giving 10 to 25 amp., may be modified by means of a specially designed chamber in which the arc plasma is constricted and carried through a circular opening in the cathode by a stream of helium. This results in a flame-like jet discharge with an estimated temperature of 10,000° K, which produces spark-like spectra. Samples in soln. may be introduced into the arc as a spray carried by a stream of argon through a hole in the anode. A preliminary test on the analysis of stainless steels for Cr and Ni gave a coeff. of variation of 2%. P. T. BEALE

308. Versatile light-weight spectrographic source unit. H. M. Davis and J. Campbell [U.K.A.E.A. (Res. Group), Woolwich Outstation, Royal Arsenal, London]. A.E.R.E. Report C/R 2605, 1959, 22 pp.—A source unit is described which is compact, mobile and inexpensive, and provides a wide range of highly reproducible working conditions. It is constructed mainly from readily available components, and the special parts required are simple to make. It can furnish discharges ranging from an energetic spark to an interrupted arc, with a repetition frequency of 50 or 100 per sec. G. S. ROBERTS

309. Characteristics of a combination discharge and its applicability in spectrochemical analysis of metals. H. E. Biber and S. Levy (U.S. Steel Corp., Monroeville, Pa.). *J. Opt. Soc. Amer.*, 1959, **49** (4), 349-355.—A source for spectrochemical analysis is described in which arc and spark discharges are combined. The stability is comparable with that of the conventional spark discharge, while the intensity, and hence the sensitivity, approach that of the arc discharge. The source can thus be used for the simultaneous determination of elements in both the low and the high concentration ranges; it has been applied successfully to the routine analysis of low-alloy steel and of tin-, zinc- and aluminium-base alloys. The vaporisation of the electrode material can be controlled to some extent independently of the spectral excitation; this may be useful in more fundamental studies of spectral excitation processes, including an understanding of the influence of extraneous elements. B. S. COOPER

310. The method of "single addition" in spectral trace analysis. I. Application to quantitative analysis. J. Świątosławska and S. Held (Inst. of Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 515-530.—The method, which is based on a single addition of the analysed substance, is discussed. The calculated and experimental results and limits of error are tabulated. The optimum experimental conditions are given.

II. Application of linear extrapolation in semi-quantitative analysis. J. Świątosławska and S. Held. *Ibid.*, 1958, **3** (3-4), 531-541.—The method of

linear extrapolation is applied in semi-quantitative spectral analysis. The systematic and random errors and the optimum conditions are discussed. H. DMOWSKA

311. Reference-beam attenuator for use in infra-red spectroscopy. R. A. G. Carrington (Shell Research Ltd., Thornton Res. Centre, Chester, England). *Spectrochim. Acta*, 1959, (2), 157-159.—A 10-bladed star wheel, driven at 2900 r.p.m., may be accurately positioned in the reference beam to give a controlled expansion of the transmission scale. The device can be used for the removal of background, which is often troublesome with solid samples, and it is generally useful in improving the accuracy when measuring transmissions below 10%. P. T. BEALE

312. A variation of the compensation technique in infra-red spectrophotometry. R. P. Manno, N. Paraskevopoulos and H. J. Matsumura (Picatinny Arsenal, N.J., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (3), 57-59.—Details are given of a simple technique in which a compound and its derivative are compared directly by placing them respectively in the reference and the sample beams of a double-beam spectrophotometer. The results of preliminary studies and the quant. application of the spectra, in which the effect of the substituent group itself and of its interaction with the parent nucleus are accentuated, are described. Comparisons of solid, liquid and solid-liquid pairs are discussed. E. G. CUMMINS

313. High-resolution infra-red ammonia spectrum. W. Kaye (Beckman Instruments, Inc., Fullerton, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1127.—The spectrum, obtained on a Beckman IR-7 prism-grating spectrophotometer, with a 10-metre adjustable path length multi-reflection Beckman cell, can be used as a measure of instrument resolution either by examining the separation of closely spaced bands or by measuring the half-band width of single isolated lines. K. A. PROCTOR

314. Optical [emission] spectra of some rare-earth and transuranic elements in the 1 to 3-micron region. I. Apparatus. L. Bovey and E. B. Steers (A.E.R.E., Harwell, England). A.E.R.E. Report AERE C/R 2827, 1959, 23 pp.—Problems associated with measurements in this region are discussed. The preferred source consisted of a tube containing a halide of the element with A or Ne at a pressure of a few torr; such tubes emit an intense spectrum when heated to 900° and excited by a magnetron oscillator operated at 2425 Mc/s. The spectrometer (illustrated) was of the Fastie-Ebert type with a focal length of 100 cm and an aperture of f/7. The light from the source was interrupted mechanically or the voltage on the magnetron was modulated at 800 c/s; the output from the lead sulphide detector was amplified by a standard 800 c/s amplifier. Details of the filters used to separate orders are given. The measurement of wavelength is considered in detail. G. J. HUNTER

315. Micro-radiography for absorption analysis. V. M. Mosley and R. W. Wyckoff (National Inst. Health, Bethesda, Md., U.S.A.). *J. Ultrastruct. Res.*, 1958, **1**, 337-348.—The projection X-ray microscope was modified for use in absorption X-ray analysis. Various wavelengths can be generated from the X-ray fluorescent radiation of various

elements. The identification of chemical elements in micro-regions of a sample is illustrated with micro-radiographs of several sectioned rocks.

CHEM. ABSTR.

316. Some practical aspects of X-ray spectrography. M. C. Lambert (General Electric Co., Hanford Atomic Products Operation, Richland, Wash.). *U.S. Atomic Energy Comm., Rep. AHW-58967*, 1959, 65 pp.—A discussion of the principal factors involved in X-ray spectrography is presented. Techniques of sample preparation, the analysis of a variety of heterogeneous samples, and other applications, such as the measurement of film thickness, are described.

NUCL. SCI. ABSTR.

317. Fluorescence X-ray spectrography—a recent analytical technique. M. C. Lambert (General Electric Co., Hanford Atomic Products Operation, Richland, Wash.). *U.S. Atomic Energy Comm., Rep. HW-58750*, 1958, 19 pp.—X-ray spectrography is applicable to both qual. and quant. determinations of all elements heavier than Na. The method is described, and its advantages and limitations are discussed. Typical analyses are mentioned, and sensitivity limits for the determination of the various elements are illustrated.

NUCL. SCI. ABSTR.

318. Elementary analysis by X-ray fluorescence spectrography. II; III. G. Baron, J. Favre and C. Raimbault (Inst. Franç. du Pétrole). *Rev. Inst. Franç. Pétrole*, 1959, **14** (4-5), 647-667.—Modifications to the apparatus previously described (Raimbault and Baron, *Ibid.*, 1958, **13**, 1253) allow the extremely soft K_{α} radiation of elements as light as Mg to be measured. Practical aspects of technique and interpretation are discussed, and several analyses are described as examples.

G. BURGER

See also Abstract—37, Interferences in flame photometry.

Thermal

319. Individual combustion of organic compounds by means of an automatic [regulator]. G. Kainz (II Chem. Inst. der Univ., Wien). *Z. anal. Chem.*, 1959, **166** (6), 427-433.—The rate of combustion of organic compounds differs and an apparatus is described in which the rate of traverse of a heating furnace along a tube containing the sample is regulated by the rate of combustion of the sample, as indicated by change in pressure of the oxygen flow into the system.

T. R. ANDREW

320. Linear voltage temperature furnace for thermal analyses. A. J. Martin and K. L. Edwards (Atomic Weapons Res. Estab., Aldermaston, Berks., England). *J. Sci. Instrum.*, 1959, **38** (4), 170-172.—The furnace, designed for operation up to 1330° in vacuum or an inert atmosphere, comprises a tubular tantalum heating element (9 in. long, 1.25 in. diam., 0.002 to 0.003 in. thick) surrounded by six concentric radiation shields of molybdenum sheet. With low heating and cooling rates a linear variation in voltage with time produces an almost linear variation in temperature. Extremely high heating and cooling rates can be obtained if required.

G. SKIRROW

321. Thermistorised apparatus for differential thermal analysis. Application for determination of thermograms of nitrate esters of cellulose and

pentaerythritol. J. M. Pakulak, jun., and G. W. Leonard (U.S. Naval Ordnance Test Station, China Lake, Calif.). *Anal. Chem.*, 1959, **31** (6), 1037-1039.—The simple, sensitive apparatus described is based on the use of two matched thermistors with their parallel shunts in adjacent arms of a Wheatstone bridge. The output from the bridge is fed to a recorder. The system is satisfactory over the temp. range from 20° to 300°.

K. A. PROCTOR

Electrical

322. Application of a stationary "hanging" mercury drop electrode in analytical chemistry. W. Kemula and Z. Kublik (Dept. of Inorg. Chem., Univ., Warsaw). *Chem. Anal., Warsaw*, 1959, **3** (3-4), 483-488.—A method for determining low concn. of Cu, Pb, Cd and Zn ($\approx 10^{-4} M$) is described. A mercury drop electrode is used as the cathode, and the polarograph registers the dissolution of the amalgams produced. The apparatus is illustrated.

H. DMOWSKA

323. Evaluation of the precision of some methods of determination of the end-point in potentiometric titrations. J. Minczewski (Dept. of Anal. Chem., Tech. Inst., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 453-462.—Phosphoric acid is titrated potentiometrically with NaOH soln., various aliquots of titrant being used. The results are interpreted graphically by several methods, those of Gran (*Analyst*, 1952, **71**, 661) and Hahn (*Anal. Chim. Acta*, 1954, **11**, 396) giving the best location of the end-point. A precision of ± 0.3 to 0.4 ml may be obtained when the difference of potential is 50 to 150 mV.

H. DMOWSKA

324. A new conception of the "dead-stop" method. G. Dušinský (State Inst. for Pharm. Res., Bratislava, Czechoslovakia). *Chem. Anal., Warsaw*, 1958, **3** (3-4), 445-451 (in German).—The small polarisation current empirically recommended by Foulk and Bawden (*J. Amer. Chem. Soc.*, 1926, **48**, 2044) is suitable for only a few titrations; in some cases, e.m.f. of several hundreds of millivolts are necessary. The values of the polarisation current for a given titration can be obtained from polarograms. As the value of the current near the end-point is a linear function of the concn., accurate values of the end-point can be evaluated graphically. With this newer concept of the dead-stop method, the technique can be applied to systems other than those involving oxidation and reduction.

J. H. WATON

325. Derivative chronopotentiometry. R. T. Iwamoto (Univ. of California Radiation Lab., Livermore, U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1062-1065.—A differential derivative technique has been developed for evaluating transition times in single-drop chronopotentiometry which can be used with poorly-defined chronopotentiograms. The limitations of the technique in investigating very dil. soln. of electroactive substances are discussed, and the characteristics and performance of several electrode systems are presented.

K. A. PROCTOR

326. (Ethylenedinitrilo)tetra-acetic acid titration of metal ions. Polarised mercury electrodes. A. E. Martin and C. N. Reilly (Chem. Dept., Univ. of N. Carolina, Chapel Hill, U.S.A.). *Anal. Chem.*, 1959, **31** (6), 992-1001.—The use of polarised

end-point detectors for EDTA titrations of metal ions and the optimum conditions for this form of titration are discussed at length. Millimolar concn. of Ca^{++} and Cu^{++} can be titrated with 0.025 M EDTA (disodium salt), using either one or two polarised mercury electrodes for end-point detection, if a small amount of Hg^{++} -EDTA, plus a suitable buffer, are initially added to the sample soln. Suitable mercury electrodes and three different methods of determining the end-point are described.

W. J. BAKER

327. Photometric iodine microcoulometer. S. Gresz (Inst. of Inorg. Chem., Polytech. Univ., Budapest, Hungary). *Period. Polytech.*, 1959, **3** (2), 105-111 (in English).—In the coulometer described, the current is measured by the electrolysis of a soln. of KI and starch in dil. H_2SO_4 , the liberated iodine being measured photometrically. It can be used to measure small currents, from 3×10^{-8} to 3 coulombs, with a max. error of 10%. It is thus possible to determine small quantities (10^{-8} to 10^{-5} g-equiv.) coulometrically. The range can be increased by replacing the iodide-iodine reaction system by, for example, the electrolytic production of KMnO_4 .

K. A. PROCTOR

328. Automatically operating, coulometric titration method for continually measuring small amounts of water in fluids. E. Barendrecht (Central Lab., Netherland State Mines, Geleen). *Nature*, 1959, **193**, 1181-1182.—The method is based on the Karl Fischer procedure, except that the iodine is generated by the anodic oxidation of a modified soln. containing HI instead of iodine, and is measured coulometrically. The titration efficiency is not 100% but is constant for a given electrolyte. An apparatus for the continuous and automatic analysis of samples is described and illustrated.

G. P. COOK

329. Amperometric titration without applied e.m.f. E. Michalski (Dept. of Inorg. Chem., Łódź Univ., Poland). *Chem. Anal.*, Warsaw, 1958, **3** (3-4), 423-430.—A system of two electrodes (reference and indicator) is used for electrometric titrations. They serve as an anode and cathode, respectively, according to the difference in potential. The end-point of the titration is given at zero current. Titration curves for KMnO_4 with a ferrous salt, of AgNO_3 with KI, and of a cerium salt with Na tartrate are given.

H. DMOWSKA

330. Resolution of electron probe micro-analysers. D. B. Wittry (Calif. Inst. Technol., Pasadena). *J. Appl. Phys.*, 1958, **29**, 1543-1549.—The minimum vol. of elements which can be analysed are limited by the size of the electron probe, by fluorescence excitation, and by the penetration and diffusion of the electrons in the specimen. With an electron accelerating voltage of ≈ 30 kV the electrons have an energy ≈ 3 times the critical excitation energy of the K or L X-ray levels of the target, and the

minimum vol. which can be analysed (in the absence of strong fluorescence effects) is ≈ 8 cu. μ for a Cu target, and is considerably larger than this for targets of low atomic number or density. It is shown that the resolution in this method of analysis can be improved without loss of statistical accuracy or increase in the time of measurement by (i) improving the quality of the electron optics and (ii) selecting the accelerating voltage and electron probe size. The vol. of the element for practical quant. analysis can thereby be made as small as 0.2 cu. μ in a Cu target. This is obtained by using slightly larger electron probes and lower accelerating voltages than those used at present.

CHEM. ABSTR.

331. Method for estimating beta-counting efficiencies. B. P. Bayhurst and R. J. Prestwood (Univ. of California, Los Alamos Sci. Lab., N.M., U.S.A.). *Nucleonics*, 1959, **17** (3), 82-86.—The plot of the counting efficiency under standard conditions against the average energy of the β -particles or positrons is a smooth curve. The average energy used is dependent on the maximum energy, the atomic number of the disintegrating nucleus and on whether the radiation consists of β -particles or positrons; a correction is applied to the maximum energy for forbidden transitions so that the standard relationships apply. The method may be used with any β -counting system, and predictions of efficiencies are accurate to $\pm 3\%$.

G. J. HUNTER

332. Synthetic mica as a monochromator for long-wavelength neutrons. A. N. Goland, J. H. Sondericker, jun., and J. J. Antal (Brookhaven Nat. Lab., Upton, N.Y., U.S.A.). *Rev. Sci. Instrum.*, 1959, **30** (4), 269-271.—Synthetic fluorophlogopite mica ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$) reflects a neutron beam which is from two to six times as intense as that from a natural mica monochromator, while requiring no appreciable sacrifice of resolution.

G. SKIRROW

333. Construction of a nuclear induction spectrometer. L. Wegmann (Sci. Instrument Div., Trüb, Täuber & Co. A.-G., Zürich). *Chimia*, 1959, **13** (1), 24-30.—The requirements for a satisfactory nuclear induction spectrometer are discussed, and the component parts are described and illustrated.

H. M.

334. Strong focusing ion source for mass spectrometer. C. F. Giese (Dept. of Physics, Univ. of Chicago). *Rev. Sci. Instrum.*, 1959, **30** (4), 260-261.—The ion source described incorporates an electrostatic quadrupole lens, in which the ions pass through a field having the potential distribution $V = \pm V_0(r^2/R_0^2)\cos 2\theta$. Starting with an ion beam 0.375 in. square, a line focus 0.60 in. long and 0.025 in. wide with a half-angle of divergence beyond the crossover of 0.034 rad. is produced.

G. SKIRROW

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.	milli-equivalent	milli-equiv.
ampere	amp.	milligram	mg
Ångström unit	Å	millilitre	ml
anhydrous	anhyd.	millimetre	mm
approximate, -ly	approx.	millimicrogram	mμg
aqueous	aq.	millimolar	mM
atmospher-e, -ic	atm.	millivolt	mV
boiling-point	b.p.	minute (time)	min.
British thermal unit	B.Th.U.	molar (concentration)	M
calorie (large)	kg-cal.	molecul-e, -ar	mol.
calorie (small)	g-cal.	normal (concentration)	N
centimetre	cm	optical rotation	α _D
coefficient	coeff.	ounce	oz
colour index	C.I.	parts per million	p.p.m.
concentrated	conc.	per cent.	%
concentration	concn.	per cent. (vol. in vol.)	% (v/v)
constant	const.	per cent. (wt. in vol.)	% (w/v)
crystalline	} cryst.	per cent. (wt. in wt.)	% (w/w)
crystallised		potential difference	p.d.
cubic	cu.	precipitate (as a noun)	ppt.
current density	c.d.	precipitated	pptd.
cycles per second	c/s	precipitating	pptg.
density	ρ	precipitation	pptn.
density, relative	d or wt. per ml	preparation	prep.
dilute	dil.	qualitative, -ly	qual.
direct current	d.c.	quantitative, -ly	quant.
distilled	dist.	recrystallised	recryst.
ethylenediaminetetra-acetic acid	EDTA	refractive index	n _D ²⁰
electromotive force	e.m.f.	relative band speed	R _B
equivalent	equiv.	relative humidity	r.h.
gram	g	revolutions per minute	r.p.m.
gram-molecule	mole	saponification value	sap. val.
half-wave potential	E _{1/2}	saturated calomel electrode	S.C.E.
hour	hr.	second (time)	sec.
hydrogen ion exponent	pH	soluble	sol.
infra-red	i.r.	solution	soln.
insoluble	insol.	specific gravity	sp. gr.
international unit	i.u.	specific rotation	[α] _D ²⁰
kilogram	kg	square centimetre	sq. cm.
kilovolt	kV	standard temp. and pressure	s.t.p.
kilowatt	kW	temperature	temp.
liquid	liq.	ultra-violet	u.v.
maximum, -a	max.	vapour density	v.d.
melting-point	m.p.	vapour pressure	v.p.
microgram	μg (not γ)	volt	V
microlitre	μl	volume	vol.
micromole	μmole	watt	W
micron	μ	wavelength	λ
milliampere	mA	weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	>	less than	<
not greater than	≥	not less than	≤
is proportional to	∝	of the order of, approximately	≈

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, e.g., Fe^{II}, Mo^V. Substances in the ionic state are represented by Na⁺, Fe²⁺, Fe³⁺, etc., for cations and by Cl⁻, SO₄²⁻, PO₄³⁻, etc., for anions.

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